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The Nature of the Soft Component of the Cosmic Radiation

C. G. MONTGOMERY AND D. D. MONTGOMERY
Bartol Research Foundation of the Franklin Institute, Swarthmore, Pennsylvania
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An inquiry is made into the nature of the corpuscular entities which possess the properties necessary to explain the soft component of the cosmic radiation on the basis of the recent theory of W. F. G. Swann. The conclusion is reached that the most likely entities are *protons* which lose energy according to the relation $-dE/dx=\lambda E+\alpha$, where α represents the energy lost per unit path by ionization, and λE the energy which goes into the production of secondaries in the amount that is actually observed in the form of showers.

SINCE the discovery of the latitude effect which demonstrated that there must be a corpuscular component of the cosmic radiation, there have been many attempts to find out what the nature of the corpuscular entities must be. The most complete treatment of this question has been given by A. H. Compton.[1] Compton has discussed the problem from the point of view that, to a large extent, the observed cosmic-ray particles are the primary entities themselves, and he has concluded that, at sea level, the hard component consists most probably of protons while the soft component may be ascribed to electrons. W. F. G. Swann[2] has discussed corpuscular theories from another point of view, namely, that the observed cosmic-ray particles are largely secondary in character, and that the number of secondary particles accompanying a primary one varies with the energy of the primary ray. If this view is adopted, then the considerations regarding the nature of the primary entities must be modified. It is the purpose of this paper to inquire into the nature of the primary entities from the point of view that the observed cosmic rays are largely secondary.

W. F. G. Swann has shown that the experimental data are well satisfied if it be assumed that the soft component of the cosmic radiation is corpuscular in nature and charged, and loses energy according to the relation $-dE/dx=\lambda E+\alpha$, where α represents the energy lost in the excitation and ionization of the atoms per unit of path, and λE is the energy which is lost by the production of secondaries. One of the numerical values of λ which results from these considerations is 0.3 per meter of water. It is our purpose to discover what the nature of the primary corpuscles must be in order that they should lose their energy according to this law with this value of λ. The only candidates which we need consider are protons and electrons, since particles of greater mass or larger charge will not be able to penetrate to any great depths into the earth's atmosphere.[1] The energy loss α is practically the same for both electrons and protons of high energy, and we cannot utilize its numerical value as a clue to the identity of the primary rays. Besides this constant energy loss, charged particles may lose

[1] A. H. Compton, Proc. Phys. Soc. **47**, 747 (1935); Rev. Sci. Inst. **7**, 71 (1936).
[2] W. F. G. Swann, Phys. Rev. **47**, 575 (1935); **48**, 641 (1935); **50**, 1103 (1936).

energy by three processes: (a) by radiation, (b) by the production of pairs of electrons, and (c) by the production of showers. The cross sections for energy loss by processes (a) and (b) have been calculated by Bethe and Heitler,[3] and Nordheim.[4] The cross section for process (b) is only about 1/137 that for process (a). Although a theoretical mechanism for the production of showers has recently been given by Heisenberg,[5] and Oppenheimer,[6] the calculations are not as yet sufficiently detailed to give a value for the energy lost in this way. However, we may utilize the observations on the frequency of occurrence of showers to derive a value for this cross section in the following manner.

Let $F(E)dE$ be the number of primary rays of energy E crossing a unit area at sea level per second. The total amount of energy going into secondaries of these rays per unit path length is then $\int \lambda EF(E)dE$, where the integral is taken over all values of the energy. Let e be the average energy of a shower ray, and $R(N)$ be the frequency distribution of showers of N rays. For $R(N)$ we may take the experimentally determined form $R(N)=\gamma Z^2/N^3$,[7] and hence

$$\int \lambda EF(E)dE=\int_2^\infty eNR(N)dN=e\gamma Z^2/2.$$

Now the total flux of primary energy through our unit area is $\int EF(E)dE$. This energy will eventually all be dissipated in the excitation and ionization of atoms below sea level. If J is the average energy lost in producing one ion pair, and $I(x)$ the observed rate of ionization per unit volume caused by cosmic radiation at a distance x below sea level, then, neglecting the small amount of ionization produced below our unit area by secondary rays which originate above this area, the flux of primary energy is given by

$$\int EF(E)dE=J\int_0^\infty I(x)dx.$$

Thus we can find λ in terms of quantities which may be measured experimentally:

$$\lambda=e\gamma Z^2/2J\int_0^\infty I(x)dx.$$

A value for γ may be estimated from experiments by counters and by ionization methods. The counter observations are uncertain, on one hand, because of the difficulties in estimating the efficiency of a particular counter arrangement, and, on the other hand, the evaluation of the ionization experiments necessitates an uncertain extrapolation to the showers of smallest size. However, the values of γ obtained from the work of various observers[7, 8] vary from 0.7×10^{-5} sec.$^{-1}$ mole^{-1} to 5×10^{-5} sec.$^{-1}$ mole^{-1}, and we may take for these purposes the value of 2×10^{-5} sec.$^{-1}$ mole^{-1}. $I(x)$ may be taken from the observations of R. A. Millikan and his collaborators,[9] and we find, for the ionization produced by the soft component below sea level, the value of 7.1×10^4 ion pairs cm^{-2} sec.$^{-1}$. Assuming J as 32.2 ev, $Z^2=52$ for air, $e=10^8$ ev, we obtain $\lambda=0.16$ per meter of water.

The values of λ for the processes (a) and (b) may be calculated from the known expressions. Table I contains the values of λ for these methods of energy loss for protons and electrons in units of meter^{-1} of water. The value of λ which is to be compared to the 0.3 m^{-1} deduced from the theory of W. F. G. Swann is the sum of the λ's for all processes of energy loss with the exception of the energy lost by ionization and excitation of atoms along the path. Thus, even if we postulate that electrons are unable to produce showers, the total, theoretical λ for electrons is too large. On the other hand, if we assume that showers are not produced by protons, the theoretical value of λ is much too small. Thus it appears that *the soft component of the cosmic radiation consists of*

TABLE I. *Values of λ in meter^{-1} of water for energy lost by various processes.*

Energy loss by	Electrons		Protons
Radiation	2.2		$2.2/(1840)^2$
Pair Production	0.0073		$0.0073/(1840)^2$
Showers		0.16	

[3] H. Bethe and W. Heitler, Proc. Roy. Soc. **A146**, 83 (1934).
[4] L. Nordheim, J. de phys. et rad. **6**, 135 (1935).
[5] W. Heisenberg, Zeits. f. Physik **101**, 533 (1936).
[6] J. R. Oppenheimer, paper delivered at the Harvard Tercentary Conference (1936).
[7] C. G. Montgomery and D. D. Montgomery, Phys. Rev. **50**, 490 (1936), and earlier references there given.
[8] H. Geiger and O. Zeiller, Zeits. f. Physik **97**, 300 (1935); J. C. Street and R. T. Young, Phys. Rev. **47**, 572 (1935).
[9] I. S. Bowen, R. A. Millikan and H. V. Neher, Phys. Rev. **44**, 246 (1933).

primary protons which lose their energy according to the law $-dE/dx=\lambda E+\alpha$, *where* λE *represents the energy loss by the production of showers.* The value of 0.16 for λ derived from shower data differs from the 0.3 required by Swann's theory only by a factor of two, well within the uncertainty of the data involved in calculating it. For example, if γ is taken as 4×10^{-5} sec.$^{-1}$ mole^{-1}, or e as 2×10^{8} ev, values well within the range of the observations, the λ calculated from shower production will agree exactly with that required by theory.

This hypothesis can explain, naturally, an east-west effect due to positively charged particles, which increases with altitude as does the soft component, although the detailed explanation of this effect is much more complicated than is suggested here. The hypothesis is not in contradiction with the recent experiments attempting to detect a proton component of the cosmic radiation,[10] since the actual number of protons passing through an area at sea level will be small compared to the number of secondary rays which accompany them. Thus, although the earth's magnetic field will affect the soft component of the radiation before it enters the atmosphere, and so produce the latitude and azimuthal effects, the cosmic-ray particles which will be observed will be, for the most part, positive and negative electrons: the shower particles which the primary protons have produced.

The recent theory of shower production of Heisenberg[5] results in the conclusion that about half of the energy lost by a primary ray in producing a shower will go into neutrinos, and it would seem necessary to take this into account by multiplying e, the energy of a shower ray, by a factor of two. However, this is not necessary, since again half, approximately, of the energy which passes through a unit area will also go into the production of neutrinos and not into the eventual production of ionization. Thus to the approximation considered here, the presence or absence of neutrinos does not influence the result.

The validity of the above choice of protons for the soft component primaries rests, of course, upon the assumption that Bethe and Heitler's theoretical formula for the radiation of fast electrons is correct for the energy range here involved. In the past, considerable doubt has been cast upon it, and several modifications[11] of the expression have been suggested. It is not our purpose to discuss these here except to point out that the recent results of Anderson and Neddermeyer[12] restore some confidence in the correctness of the formula. If the formula is proved to be invalid, however, the suitability of protons for the soft component is not affected, but we may also have to admit the possibility of electrons; electrons, however, which *do not lose energy proportionally to their energy*, and the corpuscular theory would have to be generalized to take this into account.

Thus, with due regard for the possible objections outlined above, the most probable entities which behave in a manner necessary to satisfy the requirements of the corpuscular theory of W. F. G. Swann for the soft component of the cosmic radiation are protons which produce secondaries in the numbers which are actually observed as showers. In conclusion, the authors wish to express their deep appreciation to Professor Swann for much valuable discussion, advice and criticism.

[10] C. G. Montgomery, D. D. Montgomery, W. E. Ramsey and W. F. G. Swann, Phys. Rev. **50**, 403 (1936); R. B. Brode, H. G. MacPherson, and M. A. Starr, Phys. Rev. **50**, 581 (1936); C. G. Montgomery and D. D. Montgomery, Phys. Rev. **50**, 975 (1936).

[11] J. R. Oppenheimer, Phys. Rev. **47**, 44 (1935); L. W. Nordheim, Phys. Rev. **49**, 189 (1936); W. F. G. Swann, Phys. Rev. **49**, 829 (1936).

[12] C. D. Anderson and S. H. Neddermeyer, Phys. Rev. **50**, 263 (1936).

On Multiplicative Showers

J. F. CARLSON AND J. R. OPPENHEIMER
University of California, Berkeley, California

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In I we discuss the status of the quantum theoretic formulae for pair production and radiation in the domain of cosmic-ray energies, and the relevance of these processes to an understanding of showers and bursts. In II we give a qualitative estimate of the course implied by the theory for a shower or burst built up by multiplication from a very energetic primary; we then set up the diffusion equations for the equilibrium of electrons and gamma-rays, and show how these can be simplified. In III we carry through the analytic solution of the diffusion equations, and find the distribution of electrons and gamma-rays as a function of their energy, the primary energy, and the thickness and atomic number of the matter traversed. We treat the effect of ionization losses on the shower, calculate the amount of radiation of low energy to be expected, and treat transition effects in passing from one substance to another. In IV we discuss the results of the calculations, and give a summary of the conclusions to which they lead, and the difficulties.

I

IN nuclear fields, gamma-rays produce pairs, and electrons lose energy by radiation. The formulae which have been deduced[1] from the quantum theory give for the probability of these processes values which, for sufficiently high energies, no longer depend upon the energy of the radiation. Because of this, the secondaries, produced by a photon or electron of very high energy, will be nearly as penetrating as the primary, so that the primary energy will soon be divided over a large number of photons and electrons. It is this development and absorption of showers which we wish to investigate.

The finite limiting cross sections for radiative loss and for pair production essentially limit the penetrating power of electrons and photons; as we shall see, 20 cm of Pb should absorb practically all such radiation if the primary energies are $<10^5$ Mev. From this one can conclude, either that the theoretical estimates of the probability of these processes are inapplicable in the domain of cosmic-ray energies, or that the actual penetration of these rays has to be ascribed to the presence of a component other than electrons and photons. The second alternative is necessarily radical; for cloud chamber and counter experiments show that particles with the same charge as the negative electron belong to the penetrating component of the radiation; and if these are not electrons, they are particles not previously known to physics.[2]

Direct evidence for the approximate validity of the theoretical formulae is provided by the latest studies of Anderson and Neddermeyer[3] on the energy loss and pair production of electrons of energy up to 400 Mev. This evidence is still incomplete; yet it affords absolutely no indication of a breakdown of the theoretical formulae. Since there is good evidence from the altitude and latitude curves of cosmic-ray ionization, as well as from the transition curves for showers and bursts, of a component in the cosmic rays which is strongly absorbed and yet has a very high energy, it seems of interest to investigate in detail the consequences which the theoretical formulae imply for the degradation, multiplication and absorption of such radiation. We shall find in this way a model for the building up and absorption of large showers and bursts which in many important respects agrees with what is found experimentally.[4] From this we should like to derive on the one hand a further argument for the qualitative validity of the theoretical formulae, and on the other for the often repeated suggestion that many showers are built up by a long succession

[1] An account of the results and of the theory upon which they are based may be found in Heitler's book, *The Quantum Theory of Radiation* (Oxford, 1936).

[2] Thus Williams first suggested that penetrating cosmic rays were protons, positive and negative: E. J. Williams, Phys. Rev. **45**, 729 (1934). Cloud chamber evidence would favor a particle of smaller mass.

[3] C. D. Anderson and S. Neddermeyer, Phys. Rev. **50**, 263 (1936).

[4] An account of the experimental findings on showers and bursts and their transition effects may be found in Geiger's article, "Die Sekundaer Effekte der Kosmischen Ultrastrahlung," Naturwiss. (Leipzig, 1935).

of simple elementary processes, and not by the simultaneous ejection of a huge number of particles in one elementary act.

Here a certain caution is necessary. Cloud chamber observations have shown the existence of two fairly well differentiated types of shower.[5] In one of these, and by far the more common, only electrons, positrons and γ-rays appear to take part; the shower particles are, except for those of very low energy, well collimated, with transverse momenta of the order of a few million volts; the showers can often be seen to increase in passing through matter, and typically, if they are large, have no well-defined focus. It is these showers for which our calculations will give us some understanding. In the other and rarer type of shower, transverse momenta of the order of 100 Mev are common; the shower is usually not collimated at all; heavy recoil particles are frequently seen; and the total number of particles is usually small. It is natural to ascribe these showers to the interaction of heavy and light particles, and to accept the arguments which Heisenberg[6] has advanced to show that for such processes the probability of ejection of several particles should be of the same order of magnitude as that of one. It would seem, however, that Heisenberg's attempt to interpret on this basis the larger showers and bursts as highly multiple elementary processes is without cogent experimental foundation; and we believe that in fact it rests on an abusive extension of the formalism of the theory of the electron neutrino field.

One can then believe in the applicability of the following analysis to cosmic-ray photons and electrons and their showers, only if he admits the presence of another component to which the analysis is not at all applicable, and of other types of elementary processes, which essentially involve the heavy particles and their coupling with electrons, and which find no place in this treatment.

II

We are interested then in what happens when an electron (or positron or photon) of very high initial energy passes through matter. We shall consider only the three elementary processes of pair production by photons, radiation by electrons, and ionization losses by electrons, the first two because they dominate the multiplication which makes the shower, the third because it limits the size of the shower and absorbs it. We shall not consider relatively rare multiplicative processes, such as the production by electrons of high energy electronic secondaries, the direct production of pairs by electrons, or the Compton effect. We shall suppose that all high energy particles come off forward, and neglect the angular divergence of the shower. We shall not try to treat in detail radiation of such low energy that these simplifications are invalid.

To define the probabilities of the elementary processes, we shall use simplified formulae which approximate closely to the limiting forms which the theory gives for high energies.[1]

Thus for the probability that an electron (or positron) radiate an energy in the range $E, E+\Delta E$ in passing through a thickness Δx of matter of atomic number Z, nuclear density N, we shall take

$$P\Delta x\Delta E=\frac{K\Delta x\Delta E}{E} \quad \text{with} \quad K=\frac{4Z^2e^6N}{hm^2C^5}\ln\frac{200}{Z^{\frac{1}{3}}}. \quad (1)$$

For the probability that a gamma-ray of energy E make a pair of energy E', $E-E'$, we take

$$P'\Delta x\Delta E'=(K'\Delta x\Delta E')/E; \quad E'<E;$$
$$K'/K=\sigma\sim\tfrac{7}{9}. \quad (2)$$

It is convenient to measure length in terms of a variable $t=xK$. For Pb the unit of length is $\sim\frac{1}{2}$ cm, for water it is about 0.4 m. For elements as heavy as Pb, the constants K and K' can hardly be regarded as known within 20 percent. Formula (1) is a good approximation as long as the electronic energy is >20 Mev; formula (2) begins to give too large results for $E<50$ Mev, but is off by only a factor $\frac{3}{4}$ at $E=25$ Mev. As for ionization losses, we shall suppose them to be independent of energy, and evaluate them for those energies, where their effect will be important. Thus we shall write for electrons

$$\frac{\partial E}{\partial t}=-\beta, \quad \beta=\frac{4\pi NZe^4}{KmC^2}\ln\frac{\beta}{ZRh}. \quad (3)$$

[5] Anderson and Neddermeyer, see reference 3; Brode, MacPherson and Starr, Phys. Rev. **50**, 581 (1936).
[6] W. Heisenberg, Zeits. f. Physik **101**, 533 (1936).

For Pb, β has the value 6.5 Mev. It is quite closely inversely proportional to Z.

For primary energies which are not too high, one can carry through the calculations step by step, finding how many gamma-rays are produced by the primary, how many of these are absorbed by pair production, how many gamma-rays these in turn produce. This procedure was used in computing the number of pairs theoretically to be expected in the electron traversals studied by Anderson and Neddermeyer; it has been used by Nordheim, and by Heitler and Bhabha,[7] though here with neglect of ionization losses. It clearly becomes prohibitively laborious for thicknesses and energies of the order of those involved in large showers and in bursts; and we shall try instead to solve the diffusion equations implied by (1), (2) and (3), and so obtain an insight into the course of the shower for large thicknesses and high primary energies. An extremely rough indication of what we may expect to find we can see from a quite simple argument.

Both radiation and pair production give two rays for one in the shower. Each process of this kind has about an even chance of happening in a distance $t=1$ (somewhat less than even for pair production, somewhat more for γ-radiation). Thus the order of magnitude of the total number of electrons and γ-rays to be expected at a thickness t is 2^t. The order of magnitude of the energy loss in thickness Δt is thus $\sim\frac{1}{2}\beta 2^t\Delta t$. When the integral of this is equal to the primary energy E_0, the shower will be absorbed. Thus if T is the distance to which the shower penetrates

$$\beta 2^T \sim 2E_0 \ln 2. \tag{4}$$

From this it follows that T will increase logarithmically with E_0 and that it will decrease slowly with decreasing Z; that the number of particles in the shower will increase with E_0 roughly linearly, and will be roughly proportional to Z. For showers of about 30 particles we should expect the maximum in the shower to come at $T\sim-\log_2 30\sim 5$, or a little over two cm of Pb or about 7 cm of Fe. These are in fact[4] of the order of the distances at which maxima are found for the transition curves for relatively small showers. For bursts of 1000 particles the transition maxima are found[5] at about twice as great thicknesses, as our rough estimate would suggest.

To set up our diffusion equations, let us write $\gamma(t, E)\Delta E$ for the probable number of gamma-rays to be found at a thickness t in the energy range $E, E+\Delta E$ and $\mathcal{P}(t, E)\Delta E$ for the corresponding number of electrons and positrons. Then

$$\frac{\partial\gamma}{\partial t}=-\sigma\gamma+\frac{1}{E}\int_E^{E_0}\mathcal{P}(t, \epsilon)d\epsilon, \tag{5}$$

$$\frac{\partial\mathcal{P}}{\partial t}=2\sigma\int_E^{E_0}\frac{\gamma(t, \epsilon)}{\epsilon}d\epsilon+\beta\frac{\partial\mathcal{P}}{\partial\epsilon}+\int_{[E]}^{E_0}\frac{\mathcal{P}(t, \epsilon)}{\epsilon-E}d\epsilon-\mathcal{P}(t, E)\int_{[0]}^{E}\frac{d\epsilon}{\epsilon}. \tag{6}$$

The last two terms in (6) can be combined to give the clearly finite result

$$R=\lim_{\delta\to 0}\left\{\int_{E+\delta}^{E_0}\frac{\mathcal{P}(t, \epsilon)}{\epsilon-E}d\epsilon-\mathcal{P}(t, E)\int_{\delta}^{E}\frac{d\epsilon}{\epsilon}\right\}$$

$$=-\mathcal{P}(t, E)\ln\frac{E}{E_0-E}-\int_E^{E_0}\frac{\partial\mathcal{P}}{\partial\epsilon}(t, \epsilon)\ln\left(\frac{\epsilon}{E}-1\right)d\epsilon \tag{7}$$

and give the change in pair distribution which comes directly from the radiative losses of the charged particles. The term in β gives the corresponding change from ionization losses, and the first term on the right in (6) gives the pair production by γ-rays. In (5) the first term gives the absorption of γ-rays by pair production, and the second term their replenishment by radiation. These equations are to be solved for the boundary conditions

$$\gamma(t=0, E)=0; \quad \mathcal{P}(t=0, E)=\Delta(E, E_0), \tag{8}$$

where Δ vanishes except when E is in the immediate neighborhood of E_0, and has the in-

[7] We are indebted to Dr. Nordheim for writing to us of his results. See also Heitler and Bhabha, Nature **138**, 401 (1936). We are further indebted to Heitler and Bhabha for sending us a manuscript of the paper in which they have extended these calculations. Their results differ from ours primarily because of their neglect of ionization losses; apart from this the agreement between their values and ours is excellent. We do not agree with their conclusion that these calculations make it possible to ascribe the greater part of sea-level cosmic radiation to degraded electrons and photons of high initial energy.

tegral 1. It will be convenient, however, to take $\Delta(E_0, E_0)=0$, and to choose for Δ, not a delta function, but

$$\Delta(E, E_0)=\lim_{\alpha\to\infty}\frac{\alpha^n}{E}(\ln E_0/E)^{n-1}\left(\frac{E}{E_0}\right)^{\alpha}\frac{1}{\Gamma(n)}, \qquad n\geq 4. \quad (9)$$

The reasons for this choice will be apparent as we develop the solution.

From (5) we may write

$$\mathcal{P}(t, E)=e^{-\sigma t}(\partial^2 z)/(\partial t\partial E) \text{ with } \gamma=-e^{-\sigma t}z/E. \quad (10)$$

It is not possible by differentiation to reduce (6) to a differential equation, because of the occurrence of E in the integrand of (7). We have therefore tried to replace the terms (7) by others, which would lead to a readily soluble system of differential equations, and which would still give a good representation of (7). As we shall see, we can obtain a solution in terms of integrals of elementary functions provided we write in place of (7)

$$R\to a\int_E^{E_0}\frac{\mathcal{P}(t, \epsilon)}{\epsilon}d\epsilon+b\mathcal{P}(t, E) +cE\frac{\partial\mathcal{P}}{\partial E}(t, E)+dE^2\frac{\partial^2\mathcal{P}}{\partial E^2}+\cdots \quad (11)$$

if a, b, c, d are constants. Two elementary conditions now limit their choice.

1. The number of particles leaving a given energy range by radiation must be equal to the number entering some other range.

$$\int_0^{E_0}RdE=0.$$

2. The energy lost in Δx must be equal to that appearing in the γ-rays

$$\int_0^{E_0}REdE=\int_0^{E_0}\mathcal{P}(t, E)dE.$$

If these conditions are to hold for any $\mathcal{P}$, then $c=d=0$, etc. From (1) $a+b=0$; and from (2) $a+b/2=1$; thus we must have $a=-b=2$ and

$$R=2\int_E^{E_0}\frac{\mathcal{P}(t, \epsilon)}{\epsilon}d\epsilon-2\mathcal{P}(t, E). \quad (11a)$$

The use of this form for R corresponds to assuming a uniform distribution of energy losses instead of the $1/E$ law given by (1), and renormalizing to give the correct total energy loss. The production of γ-rays is, however, treated correctly in accordance with (1); it is only the effect of these losses on the redistribution of the electrons themselves that is falsified. Since it is difficult to give an *a priori* estimate of the error thus introduced into the solution, we have used the solutions which we have obtained to compare the values of R given by (7) and by (11a). When t is not too small, most of the particles have of course an energy $E\ll E_0$. For this case we found that the two values of R agreed within less than 5 percent. It is of some interest to ask why this should be.

The answer is to be found in the circumstance that for $E\ll E_0$, our energy distribution curves for $\mathcal{P}$ follow quite closely a $1/E^2$ law as Fig. 4 shows, and as cloud chamber observations suggest that they should. For this law

$$\mathcal{P}(t, E)\sim k(t)/E^2$$

and for $E\ll E_0$, both (7) and (11a) agree in giving

$$R=-k(t)/E^2.$$

The approximation of replacing (7) by (11a) is thus a very good approximation in the range where neither t nor $\ln E_0/E$ are too small; and we shall see that it is only here that our results are of direct physical interest, because for small t and $E\sim E_0$, the fluctuations to be expected from the probable behaviors defined by $\mathcal{P}$ and γ are all-important.

Using (11a) for R, and differentiating (6) we get, if we use (10), the differential equation for z

$$\dot{z}''+(2-\sigma)\dot{z}''+2\dot{z}'/E-2\sigma z/E^2-\beta\dot{z}'''=0 \quad (12)$$

or, with $\sigma=\frac{2}{3}$,

$$\dot{z}''+2\sigma\dot{z}''+\frac{2}{E}\dot{z}'-\frac{2\sigma z}{E^2}-\beta\dot{z}'''=0. \quad (12')$$

Here primes denote differentiation with respect to E and dots with respect to t. Eq. (12′) is to be solved with the boundary conditions

$$z(0, E)=0; \qquad \dot{z}'(0, E)=\Delta(E, E_0). \quad (13)$$

III

Let us now write

$$\lambda = \ln (E_0/E)$$

and try to solve (12′) by a Laplace transformation:

$$z = 1/(2\pi i)\int_C (dy/y) e^{\lambda y} F_y(t), \tag{14}$$

where C is some suitably chosen contour in the y plane. From (12′) we then find

$$\frac{1}{2\pi i}\int_C \frac{dy}{y} e^{(2+y)\lambda}\left\{ y(y+1)\frac{\partial^2 F_y}{\partial t^2} + [2\sigma y(y+1) - 2y]\frac{\partial F_y}{\partial t} - 2\sigma F_y \right\}$$

$$= -\frac{\beta}{2\pi i E_0}\int_C dy(y+1)(y+2) e^{(3+y)\lambda}\frac{\partial F_y}{\partial t}, \tag{15}$$

where β/E_0 is a very small number. If we neglect these terms, then

$$F_y = M_y e^{\mu(y)t} + N_y e^{\nu(y)t}, \tag{16}$$

where μ, ν are the roots of

$$\kappa^2 + 2(\sigma - 1/y + 1)\kappa - 2\sigma/y(y+1) = 0,$$

$$\begin{matrix}\mu \\ \nu\end{matrix} = -\sigma + 1/y + 1 \pm [(\sigma - 1/y + 1)^2 + 2\sigma/y(y+1)]^{\frac{1}{2}} \tag{17}$$

and for $R(y) > 0$, $\mu > \nu$. The constants M_y, N_y, and the contour C must be chosen to satisfy (13).

It is clear that the integrand of (14) will have branch points in the negative half y plane, and that it will $\to 0$ as $|y| \to \infty$. We therefore choose for our contour C a closed path, consisting of a straight line $\delta - i\infty$ to $\delta + i\infty$, and the infinite semicircle from $\delta + i\infty$ through the negative half plane to $\delta - i\infty$. From (13) we get

$$\int_C dy/y e^{\lambda y} F_y(0) = 0,$$

$$\int_C dy e^{\lambda y} \partial F_y/\partial t = -2\pi i E \Delta(E, E_0). \tag{18}$$

If we multiply (18) by $e^{-y_0\lambda}$, with $R(y_0) > \delta$, and integrate over λ from 0 to ∞, we get

$$\int_C \frac{dy}{y - y_0}\frac{F_y(0)}{y} = 0, \quad \frac{1}{2\pi i}\int_C \frac{dy}{y - y_0}\frac{\partial F_y(0)}{\partial t} = -\phi(y_0)$$

$$\text{with} \quad \phi = \lim_{\alpha\to\infty}\int_0^\infty e^{-y_0\lambda}\frac{\alpha^n}{\Gamma(n)}\lambda^{n-1}e^{-\alpha\lambda}d\lambda$$

$$= \lim_{\alpha\to\infty}(1 + y_0/\alpha)^{-n}. \tag{19}$$

Since F_y and $\partial F_y/\partial t \to 0$ as $|y| \to \infty$, and have no singularities in the right-hand half-plane, this gives

$$F_y(0) = 0; \quad \partial F_y(0)/\partial t = -\phi(y). \tag{20}$$

These are the boundary conditions for F. Any other function Δ which gives an $F_y \to 0$ and $\partial F_y/\partial t \to 0$ as $|y| \to \infty$, leaves them without singularities in the half-plane $R(y) > 0$, and whose limit gives $\Delta(E, E_0) = 0$ for $E \neq E_0$, could clearly be used in place of (9). But for the treatment of ionization losses it is convenient to have the first 3 derivatives of Δ vanish as $E \to E_0$.

Let us now carry through the solution for $\beta = 0$. For this solution we write z_0, γ_0, $\mathcal{P}_0$. From (20)

$$M_y = -\phi/(\mu - \nu), \quad N_y = \phi/(\mu - \nu), \tag{21}$$

$$z_0 = -\frac{1}{2\pi i}\int_C \frac{dy}{y} e^{\lambda y}\frac{e^{\mu t} - e^{\nu t}}{\mu - \nu}\phi. \tag{22}$$

From this we can readily calculate the total energy of gamma-rays and electrons:

$$\int_0^{E_0} E dE[\mathcal{P}_0(t, E) + \gamma_0(t, E)]$$

$$= E_0 e^{-\sigma t}\frac{1}{2\pi i}\int_C \frac{dy}{y}\frac{\phi}{1 - y}\frac{(\mu y + 1)e^{\mu t} - (\nu y + 1)e^{\nu t}}{\mu - \nu}. \tag{23}$$

The integral on the right gives the residue of the integrand at $y = 1$, which is just, as $\alpha \to \infty$,

$$2\pi i e^{\sigma t} \quad \text{since} \quad \mu = \sigma, \quad \nu = -1 \quad \text{when} \quad y = 1.$$

Thus the total energy remains constant, as it should, when ionization losses are neglected. For this the condition on the constants in (11) $a + b/2 = 1$, is essential.

When t or λ are large, then (22) may most conveniently be evaluated by the saddle point method. The approximation here involved is one which corresponds closely to the limitations im-

posed upon the physical interpretation of our solution by the fluctuations which must be expected in the actual behavior of the radiation from the average behavior given by our diffusion equations. The effect of these fluctuations can be simply formulated by the physically obvious assertion that the addition or subtraction of a thickness of matter corresponding to $t\sim 1$ has an even chance of not altering the actual distribution of pairs and gamma-rays. The asymptotic form of $\mathcal{P}$, γ for large t thus gives us results whose accuracy corresponds to the applicability of the diffusion equations themselves.

The unique saddle point of the first term of the integrand of (22) lies on the positive real axis, at a point which moves out to larger y values monotonically as t/λ is increased. If we use a subscript s to indicate that functions are to be evaluated at this saddle point, then we find from this term

$$\begin{aligned} z_0 &= -(2\pi\mu_s'' t)^{-\frac{1}{2}} \frac{\exp(\lambda y_s + t\mu_s)}{y_s(\mu_s - \nu_s)}, \\ \gamma_0 &= -z_0 e^{-\sigma t+\lambda}/E_0, \\ \mathcal{P}_0 &= \mu_s y_s \gamma_0. \end{aligned} \tag{24}$$

Here $$\mu'' = \partial^2\mu/\partial y^2.$$

From the second term of (22)

$$\frac{1}{2\pi i}\int_C \frac{dy}{y}\frac{e^{\lambda y+\nu t}}{\mu-\nu}\phi$$

we obtain a contribution which remains less than $Qe^{-\frac{1}{3}t}$, where Q is independent of λ and t, as $t\to\infty$. For large t this term is thus quite negligible compared to (24).

For $\lambda\gg t$, and $\lambda\ll t$, these expressions (24) can be evaluated analytically. Thus (writing $\sigma=2/3$).

For $\lambda\gg t$

$$\begin{aligned} z_0 &= 2^{-2}\pi^{-\frac{1}{2}}\lambda^{-\frac{1}{4}}\exp\left[\tfrac{1}{3}t+3^{\frac{1}{2}}\lambda^{\frac{1}{2}}t^{\frac{1}{2}}\right], \\ \mu_s y_s &= 2\cdot 3^{-\frac{1}{2}}\lambda^{-\frac{1}{2}}t^{\frac{1}{2}}, \end{aligned} \tag{25}$$

and for $\lambda\ll t$,

$$\begin{aligned} z_0 &= 2^{-8/3}\pi^{-\frac{1}{2}}3^{\frac{1}{4}}t^{-\frac{1}{4}}\lambda^{-\frac{1}{4}}\exp\left[3\cdot 2^{-\frac{1}{3}}\lambda^{\frac{1}{3}}t^{\frac{1}{3}}\right], \\ \mu_s y_s &= 2^{-\frac{1}{3}}\lambda^{\frac{1}{3}}t^{-\frac{1}{3}}. \end{aligned} \tag{26}$$

For intermediate values we give a plot of y_s against λ/t, from which (24) may be evaluated. It should be observed that $\mu_s y_s$ gives directly the ratio of $\mathcal{P}_0$ to γ_0, and that it never exceeds $2/3$. At any energy and thickness $t>1$, there are always more γ-rays than electrons.

The solution we have given can be readily extended to diffusion equations with R of the general form (11); only the dependence of μ and ν on y becomes more complicated.

For the treatment of the ionization losses given by the terms in β, it is simplest to return to (14), and write instead

$$z=\frac{1}{2\pi i}\int_C \frac{dy}{y}e^{\lambda y}\left[F_y^{(0)}(t)+\frac{\beta}{E}F_y^{(1)}(t)+\frac{\beta^2}{E^2}F_y^{(2)}(t)\cdots\right] \tag{27}$$

and leave the contour C unaltered. If for $F_y^{(0)}(t)$ we take (16), (21), then (12′) gives, for the first order terms in β.

$$\begin{aligned} &\frac{\partial^2 F_y^{(1)}}{\partial t^2}+2\left(\sigma-\frac{1}{y+2}\right)\frac{\partial F_y}{\partial t}-\frac{2\sigma}{(y+1)(y+2)}F_y^{(1)} \\ &=\frac{1}{2\pi i}\frac{y}{(y+1)(y+2)}\int_C \frac{dy'(y'+1)(y'+2)}{y'-y} \\ &\qquad\times\frac{\mu(y')e^{\mu(y')t}-\nu(y')e^{\nu(y')t}}{\mu(y')-\nu(y')}\phi. \end{aligned} \tag{28}$$

The general solution of this is

$$\begin{aligned} F_y^{(1)}(t)/y &= A_y e^{\mu(y)t}+B_y e^{\nu(y)t}+C_y e^{\mu(y+1)t} \\ &\quad +D_y e^{\nu(y+1)t}, \end{aligned} \tag{29}$$

where

$$\begin{aligned} A_y &= \phi\frac{\mu(\sigma+\mu y)(y+1)(y+2)}{2(2\sigma+\mu y)(\mu-\nu)}, \\ B_y &= -\phi\frac{\nu(\sigma+\nu y)(y+1)(y+2)}{2(2\sigma+\nu y)(\mu-\nu)}, \end{aligned} \tag{29a}$$

and where C_y and D_y must be chosen to maintain the boundary conditions (13), which require

$$\begin{aligned} C_y &= \frac{A_y\mu(y)+B_y\nu(y)-\nu(y+1)(A_y+B_y)}{\nu(y+1)-\mu(y+1)}, \\ D_y &= \frac{A_y\mu(y)+B_y\nu(y)-\mu(y+1)(A_y+B_y)}{\mu(y+1)-\nu(y+1)}. \end{aligned} \tag{29b}$$

For $R(y)>-1$, C_y and D_y are analytic, except for a simple pole of C_y at

$$y_p=(3-\sqrt{73})/8\sim-0.69$$

and a simple pole of D_y at

$$y_p'=(3+\sqrt{73})/8\sim1.44.$$

The terms of order β in (27) may then be written

$$\frac{\beta}{E_0 2\pi i}\int_C dy e^{(1+y)\lambda}[A_y e^{\mu(y)t}+B_y e^{\nu(y)t}+C_y e^{\mu(y+1)t}+D_y e^{\nu(y+1)t}]. \quad (30)$$

For large λ and t only the term

$$\frac{\beta}{E_0 2\pi i}\int_C dy e^{(1+y)\lambda}A_y e^{\mu(y)t}=\frac{\beta}{E 2\pi i}\int_C dy A_y e^{\lambda y+\mu t} \quad (31)$$

is important.

For the second and fourth terms in (30) we can again show that they remain less than

$$\frac{\beta}{E_0}Qe^{\lambda-2/3t} \quad \text{as } t\to\infty,\ \lambda\to\infty$$

and are therefore negligible.

The term

$$\Gamma=\frac{\beta}{E_0 2\pi i}\int_C dy C_y e^{(1+y)\lambda+\mu(1+y)t}$$

may be evaluated by deforming the contour C to pass through the saddle point at

$$y_s=-1+y_s.$$

If we call the path taken along a line parallel to the imaginary axis through y_s, Σ then

$$\Gamma=\frac{\beta}{2\pi i E_0}P\int_\Sigma dy C_y e^{(1+y)\lambda+\mu(1+y)t}+\frac{\beta}{E_0}\vartheta(y_s-y_p)G_p e^{(1+y_p)\lambda+\mu(1+y_p)t}$$

where
$$\vartheta(x)=\begin{cases}0 & x>0\\ \frac{1}{2} & x=0\\ 1 & x<0\end{cases}$$

and
$$G_p=\lim_{\epsilon\to0}(\epsilon C_{y_p+\epsilon}).$$

Each of the terms in Γ gives a contribution negligible for $\lambda\to\infty$ compared to (31). From the saddle point integral we get a contribution

$$<Q(\lambda,t)\frac{\beta}{E_0}e^{y_s\lambda+\mu_s t},$$

where Q is an algebraic function of λ and t; from the residue we get

$$<Q_1\frac{\beta}{E_0}e^{y_s\lambda+\mu_s t+(1+y_p)\lambda}$$

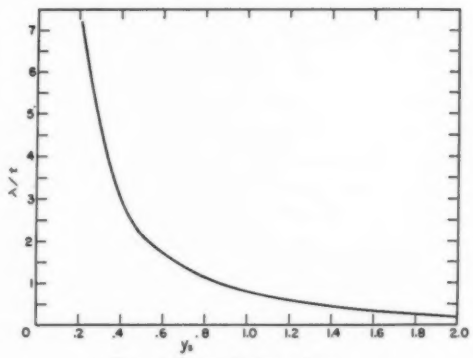

FIG. 1. Plot of λ/t against y_s.

with Q_1 a constant. Both of these are small compared to the term

$$\frac{\beta}{E_0}(2\pi\mu_s''t)^{-1/2}A_{y_s}e^{(1+y_s)\lambda+\mu_s t},$$

which we get from the saddle point integral (31).

From (31), and the application of the saddle point method to the integral occurring in it, we can readily see by what factors the values of z_0, γ_0, $\mathcal{P}_0$ given in (24) must be modified:

$$z=z_0(1-\beta\tau_s/E);\quad \gamma=\gamma_0(1-\beta\tau_s/E);$$
$$\mathcal{P}=\mathcal{P}_0(1-\beta(1+1/y_s)\tau_s/E);$$
$$\mathcal{P}=\gamma\mu_s y_s(1-\beta\tau_s/y_s E), \quad (32)$$

where
$$\tau=\frac{y(y+1)(y+2)(\sigma+\mu y)}{2(2\sigma+\mu y)}.$$

From (24) and (32) we can thus give $\mathcal{P}$, γ as functions of t and E. The ionization correction still further increases, of course, the proportion of γ-rays in the radiation.

From (32) we see that our approximate calculation of the effect of ionization losses is based upon the smallness of β/E. This parameter is about 12 percent for Pb, 35 percent for Fe, at $E=50$ Mev. Clearly the treatment here given is limited to energies $E>\beta$, but within this limit it can tell us what the effect of these losses will be.

In fact (22) and (31) give the first two terms in the asymptotic expansion in β/E of a solution of (12′):

$$z=-\frac{1}{4\pi^2}\int_C\frac{dy}{y}\frac{e^{\mu t+\lambda y}}{\mu-\nu}\phi\Gamma(-y)\int_S ds(-s)^y e^{-s}\times{}_2F_1\left(y,y+2;y+1+g;-\frac{\beta\mu y g s e^\lambda}{2\sigma E_0}\right). \quad (33)$$

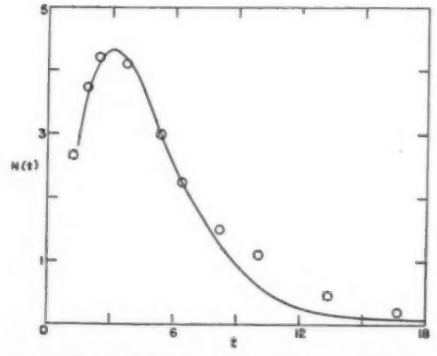

FIG. 2. Plot of total number of electrons $N(t)$ against t, for air, $E_0=2500$ Mev, computed from (36). The circles are from the experimental results of Pfotzer,* on the variation of vertical coincidence counting rate in the upper atmosphere, at magnetic latitude $\sim 50°$N. At this latitude the earth's field will just admit electrons of energy 2500 Mev. The deviations from the curve for $t>8$ may indicate the presence of some electrons of higher energy, as well as a penetrating component.

Here the contour S in the s plane is a simple loop from $+\infty$ counterclockwise around the origin and back to $+\infty$; ${}_2F_1$ is the hypergeometric series and

$$g=\sigma(1+y)/(\sigma+\mu y).$$

That (33) is a solution of (12′) may be verified by direct substitution. It is not of course the solution satisfying the boundary conditions (13); but an iteration of the arguments just given in connection with (31) indicates that the terms which must be added to satisfy (13) give for $t>1$, $E\ll E_0$, a negligible contribution.

For heavy elements such as Pb, (31) gives an adequate approximation to (33) for all energies high enough to make the use of (2) permissible: the pair production formulae break down before the ionization correction becomes very large. For light elements, for the atmosphere, we may apply (33) for $E<\beta$. To do this we use the analytic continuation of the hypergeometric series, and evaluate the integral over y by the saddle point method. For $E/\beta<1$ we thus find

$$\gamma(E,t)=e^{\lambda_\beta y_s+(\mu_s-\sigma)t}\frac{(2\pi\mu_s''t)^{-\frac{1}{2}}}{y_s(\mu_s-\nu_s)}\times\frac{\Gamma(1+y_s+g_s)}{\Gamma(1+y_s)\Gamma(2+y_s)\Gamma(1+g_s)}\frac{1}{E},$$
$$\mathcal{P}(E,t)=\frac{2\sigma E}{\beta}\gamma(E,t)\ln\frac{\beta}{E}. \tag{34}$$

* Zeits. f. Physik **102**, 41 (1936), Fig. 1, p. 42.

Here $\lambda_\beta=\ln(2\sigma E_0)/(\beta\mu_s y_s g_s)$; and the saddle point y_s is given as the real positive root of

$$\frac{d}{dy}\left\{y\ln\frac{2\sigma E_0}{\beta\mu y g}+\mu t\right\}=0 \tag{35}$$

and may be found from Fig. 1.

The energy dependence of γ and $\mathcal{P}$, which for $E>\beta$ is roughly given by k/E^2, becomes, if $E<\beta$, k_1/E, $k_2\ln\beta/E$, respectively. The increase in γ and $\mathcal{P}$ with decreasing energy will be still further reduced at still lower energies by the absorption of the γ-rays by Compton effect. The total number of electrons in the range $0-\beta$ depends upon β essentially as

$$e^{\lambda_\beta y_s}$$

and its maximum as a function of t is quite closely inversely proportional to β or proportional to Z.

The total number of electrons is easy to compute from (33):

$$N(t)=\int_0^{E_0}\mathcal{P}(E,t)dE=-e^{-\sigma t}\dot{z}(E=0,t)$$
$$=\frac{\mu_s(2\pi\mu_s''t)^{-\frac{1}{2}}}{y_s(\mu_s-\nu_s)}\frac{\Gamma(1+y_s+g_s)}{\Gamma(1+y_s)\Gamma(2+y_s)\Gamma(1+g_s)}\times e^{\lambda_\beta y_s+(\mu_s-\sigma)t}, \tag{36}$$

where y_s is given again by (35). The maximum value of $N(t)$ occurs for values of t slightly smaller than λ_β. We give Fig. 2 a plot of $N(t)$ against t, for water, for which we have taken $\beta=90$ Mev, and t is measured in units of $\sim 0.4m$. The primary energy is $\sim 2.5\times 10^3$ Mev. The maximum of N occurs at about 1.2 meters. It would seem probable that the latitude sensitive transition effects of the cosmic-ray ionization in the upper atmosphere are to be interpreted on this basis.

It is futile to apply (33) to elements as heavy as Pb, because for energies of the order of β the radiative formulae (1), (2) and the diffusion equation based on them become quite wrong. As is well known, the actual behavior of radiation in the range 1–25 Mev in Pb is extremely complicated. Since the absorption coefficient for γ-rays has a minimum value which for Pb lies at about 3 Mev, we know that for sufficiently great thicknesses of matter γ-radiation of roughly this energy will predominate over γ-rays of higher or

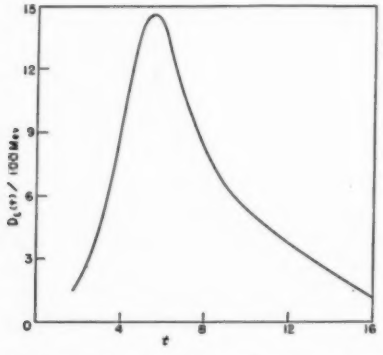

FIG. 3. A plot of the energy degraded into radiation of energy <25 Mev per unit t, against t. The plot is for Pb, $E_0=2\times10^4$ Mev. The abscissae are in units of $\frac{1}{2}$ cm, the ordinates in units 100 Mev. The number of low energy electrons to be expected at t is roughly 0.15 $D_{25}(t-3)$.

lower energy and over electrons of all energies. A rough estimate of the number of low energy electrons we can get by computing the total energy degraded into the low energy region per unit thickness. Let us call the energy so degraded into an energy region $0<E<\epsilon$, $D_\epsilon(t)$. This energy has ultimately to be absorbed by the ionization losses of electrons. The number of electrons which in a distance $t=1$ would lose by ionization an energy $D_\epsilon(t)$ is $1/\beta D_\epsilon(t)$; it must be remembered, however, that because of the relatively great penetration of the low energy gamma-rays (amounting for Pb to $t=3$–4), the low energy electrons actually present in the radiation at some fixed thickness $t=T$ must be evaluated, not from $D_\epsilon(T)/\beta$, but from some appropriately retarded value $D_\epsilon(T-r)/\beta$, where r gives the effective mean penetration of the low energy radiation, and may be of the order of 2–3 for Pb. It is in this sense that the curves we give for $D_\epsilon(t)$ are to be interpreted. For the interpretation of observations made with the high pressure, thick-walled ionization chambers which are used in the study of bursts, the variation of $D_\epsilon(t)$ with t should itself give a valid estimate of the probable variation of the recorded size of the burst with absorber thickness.

The calculation of $D_\epsilon(t)$ is straightforward. The total energy lost by the radiation of energy $>\epsilon$ per unit t is

$$D^{(1)}(t)=-\frac{d}{dt}\int_\epsilon^{E_0}[\mathcal{P}(E,t)+\gamma(E,t)]EdE. \quad (37)$$

The part of this which is accounted for by ionization losses is

$$D_\epsilon^{(2)}(t)=\int_\epsilon^{E_0}\beta\mathcal{P}(E,t)dE. \quad (38)$$

Then $$D_\epsilon(t)=D_\epsilon(t)^{(1)}-D_\epsilon(t)^{(2)}. \quad (39)$$

In this way we find, from (39), (32) and (24)

$$D_\epsilon(t)=-e^{-\sigma t}z_0\left\{\frac{(\mu_s-\sigma)(1+\mu_s y_s)}{1-y_s}\epsilon\right.$$
$$\left.-[(\sigma-\mu_s)[1+(1+y_s)\mu_s]y_s^{-1}\tau+\mu_s]\beta\right\}. \quad (40)$$

Here z_0 is given by (24), and is to be evaluated, as are μ_s, y_s and τ, for $E=\epsilon$, $\lambda=\ln E_0/\epsilon$, $t=t$. It will be observed that the effect of the terms in β in (40) is to increase $D_\epsilon(t)$ when $\lambda\gg t$, and to decrease it when $\lambda\ll t$. We give in Fig. 3 a plot of $D_\epsilon(t)$ for Pb, $\epsilon=25$ Mev, $E_0=2\times10^4$ Mev.

Let us now restrict ourselves to $E>\beta$, and ask how the shower will be altered by changes in the initial radiation.

A. If the incident radiation is a γ-ray of energy E_0 and not an electron, the boundary conditions (20) must be altered to

$$F_s(0)=\phi y; \qquad \partial F_s(0)/\partial t=0. \quad (41)$$

This gives us

$$z_{0[\gamma]}=\frac{1}{2\pi i}\int_C\frac{\nu e^{\mu t}-\mu e^{\nu t}}{\mu-\nu}dy e^{\lambda y}\phi, \quad (42)$$

from which it follows that for $t>1$, the number of gamma-rays and electrons will be changed by a factor $-\nu_s y_s$ from the values given by (32). This factor varies from 0.6 to 1.6 over the range of values of t/λ for which the shower is appreciable. The course and magnitude of the shower will thus depend very little on whether it is started by an electron or a gamma-ray. The maximum of the shower will come for very slightly higher t values when it is initiated by a γ-ray.

B. If the incident radiation is a group of m electrons of energy E_0/m, then from (24)

$$\mathcal{P}_{0[m]}=m^2\mathcal{P}_0(\lambda-\ln m,t);$$
$$\gamma_{0[m]}=m^2\gamma_0(\lambda-\ln m,t) \quad (43)$$

and insofar as $\mathcal{P}(\lambda, t)$ is quite closely of the form $k(t)e^{-2\lambda}$, for small variations of λ,

$$\mathcal{P}_{0[m]} = \mathcal{P}_0$$

for small m, and the shower will be substantially the same as if one electron of energy E_0 had started it.

C. As long as we neglect the ionization terms, we can get no "transition effects" when a shower, built up in one substance, passes into another. But the terms in β do give us such effects, in apparent qualitative agreement with what is found experimentally. Let the radiation go a distance t_1 (measured in units approximate to the first substance) in (1), and then a distance t_2 (in units for (2)) in (2). Then the terms independent of β in z are, for $t_1+t_2>1$.

$$z_0 = -\frac{1}{2\pi i}\int_C \frac{dy}{y}\,\phi\,\frac{e^{\lambda y+\mu(t_1+t_2)}}{\mu-\nu}. \qquad (44)$$

The boundary conditions

$$\mathcal{P}(E, t_1) \quad \text{in} \quad (1) = \mathcal{P}(E, t_1) \quad \text{in} \quad (2);$$
$$\gamma(E, t_1) \quad \text{in} \quad (1) = \gamma(E, t_1) \quad \text{in} \quad (2)$$

give then, for $t_1>1$, for the terms in z proportional to β:

$$\frac{1}{2\pi i}\int_C dy\phi e^{\lambda(y+1)}\Big\{\beta_2 A_y e^{\mu(y)(t_1+t_2)}$$
$$+(\beta_1-\beta_2)A_y e^{\mu(y)t_1}\Big[\frac{\mu(y)-\nu(y+1)}{\mu(y+1)-\nu(y+1)}e^{\mu(y+1)t_2}$$
$$-\frac{\mu(y)-\mu(y+1)}{\mu(y+1)-\nu(y+1)}e^{\nu(y+1)t_2}\Big]\Big\}. \qquad (45)$$

which for $t_2=0$ is just the ionization correction appropriate to (1), and which for $t_2\to\infty$ approaches that appropriate to (2). If $Z_1>Z_2$; $\beta_1<\beta_2$ and $\mathcal{P}$ is decreased by the transition; if $Z_2>Z_1$, $\mathcal{P}$ is increased. The transient terms which give the transition fall off, relative to the main terms, as

$$e^{[\mu(y_s+1)-\mu(y_s)]t_2} \quad \text{and} \quad e^{[\nu(y_s+1)-\nu(y_s)]t_2}.$$

Thus the second term will be damped out for $t_2\sim\frac{1}{2}$, but the first term will persist until $t_2\sim 1.5-2$, the transition thickness is therefore of this order of magnitude. For $E_0=2\times10^4$ Mev, $t_1=6$ the transition from Fe to Pb should increase the number of electrons with energy >50 Mev by about 35 percent.

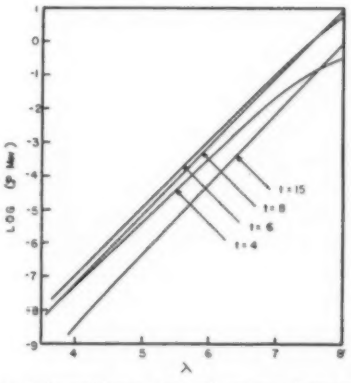

FIG. 4. A logarithmic plot of energy distributions for shower electrons, made for Pb, $E_0=1.5\times10^5$ Mev and $t=15$, $t=8$, $t=6$, and $t=4$. Abscissae are $\lambda=\ln E_0/E$; ordinates are natural logarithms of $\mathcal{P}$ measured in (Mev)$^{-1}$. A straight line of slope 2 would correspond to a $1/E^2$ distribution law.

It must be remembered that the actual transition effects observed are complicated by the fact that the high energy radiation which produces the showers is to some extent being regenerated in the material in which the showers are formed.

IV

In Fig. 4 we give typical energy distribution curves for the pairs, for Pb, and a primary energy of 1.5×10^5 Mev for $t=15$, 8, 6, 4. In the neighborhood of $\lambda=8$, the ionization corrections are appreciable, but for $\lambda<6$ the curves will hold for all substances. It will be observed that these curves follow quite closely what we would get from a distribution law k/E^2; thus except for $t=4$ they may all be represented by a law of this form in which the exponent of E never differs from -2 by more than five percent. In fact this law gives a very good approximation to the energy distribution for $t>.7\lambda$, and for all energies $E\ll E_0$ but $\gg\beta$. We have already pointed out that it is for this reason that the simplification of the diffusion equations made in replacing (7) by (11) is permissible. Cloud chamber studies[8] of the energy distribution of shower electrons seem to fit this law quite well for $E>25$ Mev, but the experi-

[8] C. D. Anderson and S. Neddermeyer, Int. Conf. Physics, London 171 (1934).

mental conditions here are clearly not such as to make this agreement very significant.

Because of the form of the distribution law, a plot of $\mathcal{P}E$ will give a good estimate of the total number of electrons to be expected with energies $\geq E$. For Pb, $E=50$ Mev, and several values of E_0 varying from 2700 Mev up to 1.1×10^6 Mev we give such plots against t (Fig. 5). The rapid increase with E_0 of the total number of particles, and the slow shift in the position of the maximum, confirm the qualitative arguments of §2. We would like to interpret in terms of this shift the well-known observation that the optimum transition thickness for bursts is considerably larger than for showers. In fact, the agreement between the experimental values of the optimal transition thicknesses (~2 cm Pb for showers, ~5 cm Pb for bursts) with the position of the maxima of these curves, seems to us a strong argument for the correctness of the model we are treating, and of the validity of the high energy formulae we have used. In particular the experiments of Nie,[9] in which it is shown that a burst generated in a suitable layer of matter may sometimes have its magnitude very much increased by the interposition of a few cm of Pb find a very natural interpretation in terms of these theoretical curves. It must be remembered, however, that the experimental transition curves, which give the dependence on t of the probability of finding a shower or burst whose magnitude exceeds a lower limit defined by the experimental arrangement are not strictly comparable with the curves of Fig. 5 which give the variation, for fixed E_0 of the probable number of electrons.[10] For in making this comparison the initial distribution of the radiation over E_0 must clearly be taken into account. We want here, too, to point out that the actual behavior of the radiation will fluctuate about that given by our curves, and that the order of magnitude of the probable fluctuations can be estimated by shifting the curves by $\Delta t\sim\pm1$.

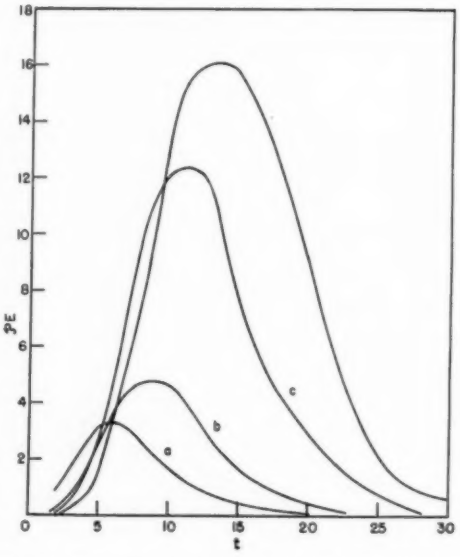

FIG. 5. Plots against t of $\mathcal{P}\cdot E$ for $E=50$ Mev in Pb. (a) $E_0=2.7\times10^3$, (b) $E_0=2\times10^4$, (c) $E_0=1.5\times10^5$; (d) $E_0=1.1\times10^6$. Abscissae are in units of $\frac{1}{3}$ cm; ordinates in units of 1, 4, 10, and 50 for (a), (b), (c) and (d), respectively. These plots also give the number of electrons of energy $\geq$50 Mev to be expected as a function of t.

The application of our methods to E_0 as low as 2700 Mev may seem unjustified. Here our results, however, agree reasonably with those computed by Bhabha and Heitler[11] with neglect of ionization losses and of processes of high order. For 50 Mev the inclusion of ionization losses reduces the number of electrons to be expected by 15–20 percent.

It may be helpful to give a brief summary of the general results. For any absorber we measure length (t) in units which are proportional, roughly, to $Z^2\rho/A$, where Z is the nuclear charge, A the atomic weight, and ρ the density, and we define the characteristic energy β (see (3)), which varies about like $1/Z$. Then,

(1) The number of electrons per unit energy is about inversely proportional to the square of the energy, as long as $\beta<E\ll E_0$, $t>\frac{1}{2}\lambda$.

(2) For given energy and $t>1$, there are always more γ-rays than electrons; where the

[9] Nie, Zeits. f. Physik **99**, 776 (1936).

[10] When counters are used to detect showers, the angular divergence of the shower rays is necessarily exploited. If the theory here developed is at all correct, most of these rays must have a relatively low energy, of the order of several million volts. In fact only cloud chamber observation can tell us much about radiation of much higher energy.

[11] Reference 8. Heitler and Bhabha give for $E_0=2.7\times10^3$ Mev, a value $\mathcal{P}E=4$, maximum for $t=4$; we get $\mathcal{P}E=4.5$ at $t=4$. This discrepancy, and the fact that we find the maximum at $t\sim5$, are both in the direction to be expected from the effects of higher order processes.

shower is near its maximum, this ratio varies from 1.5–2.

(3) For $E \gg \beta$, the distribution curves plotted against t are the same for all absorbers.

(4) The number of particles of energy greater than $E_1 > \beta$ passes through a maximum for a value of t which increases logarithmically with E_0/E_1 and is always quite close to $\ln_2 E_0/E_1$.

(5) The maximum number of particles with an energy less than some small multiple of β is attained for values of t which are slightly smaller than $\ln E_0/\beta$, and decrease slowly with decreasing Z. The total number of particles of energy in this range is about inversely proportional to β, or proportional to Z.

(6) The maximum size of the shower is limited only by E_0 with which it increases not quite linearly: thus an increase in E_0 by a factor of 100 gives an increase in shower size of about 70.

(7) If the initial energy E_0 is in an incident γ-ray, or is divided among a few electrons and gamma-rays, the course of the shower will be essentially unaltered.

(8) Passage of a shower from one material (1) to another (2) will increase the size of the shower if $Z_2 > Z_1$, decreases it if $Z_1 > Z_2$. The transition takes place in a thickness $t_2 \sim 1\frac{1}{2}$. All of these results apply only for energies E_0 above 10^9 Mev.

In this paper we have altogether neglected the question of how such high energy electrons and γ-rays can get down through the atmosphere. How serious this difficulty is we can see from (32), which tells us that for every electron of energy $\sim 2 \times 10^5$ Mev which hits the earth vertically, only 0.15 electron of energy >550 Mev will survive at the earth's surface. This difficulty is made even sharper when we consider the form of the shower curves for great thicknesses $t > 30$, or the showers and bursts reported under very great thicknesses of absorber. In fact, although when we go up far in the atmosphere, the showers, and still more markedly, the bursts, increase more rapidly than the total cosmic-ray ionization, below the atmosphere they do not fall off much more rapidly than this ionization. This suggests that, in addition to primary electrons and perhaps γ-rays, which are able to produce multiplicative showers directly, there is another cosmic-ray component, slowly absorbed, which is responsible for the continuation of the showers under thicknesses of absorber to which no electron or photon can itself penetrate. Some suggestions which we think relevant to the solution of this problem will be discussed in another paper.

Ionization of Air by γ-Rays as a Function of Pressure and Collecting Field II

I. S. BOWEN, *California Institute of Technology, Pasadena, California*
AND
EVERETT F. COX, *Colgate University, Hamilton, New York*

(Received January 2, 1937)

The γ-ray ionization current measurements in air at high pressures made by Erikson and by Clay and Van Tijn are shown to be largely modified by volume recombination at collecting fields below about 400 volts per cm. The Jaffé theory of columnar ionization does not explain the observed variation of ion current when it is applied over a wide range of collecting fields to data free from volume recombination.

IN 1932 one of the authors made ionization current measurements which were published under the above title.[1] Shortly after this Zanstra and Clay[2] called attention to earlier measurements made by Erikson[3] in 1908. Later Zanstra[4] applied the Jaffé theory of columnar ionization to explain the curves obtained by Erikson, and Clay[5] and Van Tijn made new measurements to which the formula developed by Zanstra was applied.

In the discussion of ion current measurements three types of recombination which prevent the collection of all ions formed are usually considered, namely: (a) preferential, i.e., recombination of the electron with the particular ion from which it was ejected, (b) columnar (called initial by some authors), i.e, recombination with a positive ion in the same β-ray track as the ion from which the electron was ejected, (c) volume, i.e., recombination with any positive ion. Obviously in processes (a) and (b) the probability of recombination of a given electron is independent of the number of tracks formed in the ionization chamber. Consequently if the pressure is kept constant, so that the number of ions per track does not vary, the fraction of ions collected is independent of the total ionization. On the other hand in process (c), i.e., volume recombination, the probability of recombination of a given electron is proportional to the number of positive ions in the gas. This type of recombination is therefore negligible at low rates of ionization, such as those found in measurements of cosmic-ray ionization, but becomes prominent at higher rates where it shows its presence by the variation in the fraction of the ions collected as the rate of ionization is changed.

The measurements made by Bowen were undertaken primarily to elucidate the behavior of cosmic-ray electrometers which use gases at high pressure. Consequently great care was taken to eliminate volume recombination. This was done by the use of a very weak source of radiation which produced a fairly uniform ionization of only 121 ions per cc per sec. per atmosphere. Furthermore at the two highest pressures used tests for the presence of volume recombination were made by taking a complete set of additional measurements when the ionization was reduced to 23.4 ions per cc per sec. per atmosphere. Similar precautions for the elimination of volume recombination were taken by Cox[6] in his studies of ionization in other gases than air.

On the other hand Erikson, who did not attempt to eliminate volume recombination, used ionization rates of from 2×10^5 ions per cc per sec. per atmosphere at points of the ionization chamber farthest from the radium to 10^7 ions for points nearest it. Clay and Van Tijn, according to a letter to one of the authors correcting their Table I, used an average of 2.7×10^4 ions per cc per sec. per atmosphere.

Neither Erikson nor Clay and Van Tijn tested for the presence of volume recombination by varying the average ionization used. Fortunately their collecting field and pressure ranges overlapped those of Bowen and consequently such a test can be made by superimposing their curves

[1] I. S. Bowen, Phys. Rev. **41**, 24 (1932).
[2] H. Zanstra and J. Clay, Phys. Rev. **41**, 679 (1932).
[3] H. A. Erikson, Phys. Rev. **27**, 473 (1908).
[4] H. Zanstra, Physica **2**, 817 (1935). See also, B. Gross, Zeits. f. Physik **78**, 271 (1932) and W. R. Harper, Proc. Camb. Phil. Soc. **28**, 219 (1932) and **29**, 149 (1933).
[5] J. Clay and M. A. Van Tijn, Physica **2**, 825 (1935).
[6] E. F. Cox, Phys. Rev. **45**, 503 (1934).

on Bowen's curves obtained at low rates of ionization. This is done in Fig. 1 where the number of ions collected is plotted against the logarithm of the collecting field for the pressures nearest 95 atmospheres used by each observer. All of the curves are reduced to the same scale by expressing the number of ions collected as the fraction of the number collected at 1000 volts per cm. Comparing first Bowen's curves at 23.4 ions and 121 ions it is seen that lack of superposition, indicating the presence of volume recombination at the higher ionization rate, sets in at a collecting field of 10 to 15 volts per cm. Likewise the curves obtained by the other observers using high rates of ionization definitely drop below the low ionization curves at 400 to 800 volts per cm, thus indicating the presence of volume recombination at all collecting fields below this. Similar results are obtained at other pressures although the collecting field at which volume recombination becomes negligible varies with the pressure.

The results of Erikson and Clay and Van Tijn are therefore not directly applicable to the problem of cosmic-ray ionization chambers which normally operate with collecting fields far below 400 volts per cm. Furthermore one is not justified in applying the Jaffé formula for columnar recombination except to points that fall in the range which is free from volume recombination, i.e., in Erikson's data to points from 513 to 1223 volts per cm at 140 atmospheres and from 365 to 1288 volts per cm at 40 atmospheres, and in Clay and Van Tijn's data from 817 to 4917 volts per cm. On the other hand Bowen's ionization currents obtained at an ionization rate of 23.4 ions per cc per sec. per atmosphere are quite certainly free from volume recombination over the range from 6.2 to 1009 volts per cm. Fig. 2 represents the application of the Jaffé theory to these results in the above ranges. Following Zanstra the abscissa is his $f(x)$ while the ordinate is proportional to the reciprocal of the ion current collected. As in Fig. 1 the unit of current is taken as the current collected with a field of 1000 volts per cm. When plotted in this way all points obtained at a given pressure should fall on a straight line according to the Jaffé theory. The curves are apparently linear over the small ranges of the collecting fields available in Erikson's data where the field varies by a factor of about 3 and in Clay and Van Tijn's data where the range is a factor of 6. On the other hand the linearity breaks down completely in the range in the field of a factor of 160 available in Bowen's data. This breakdown is still more striking if Clay and Van Tijn's points are combined with those of Bowen at the same pressure thus extending the range to a factor of 800 in the collecting field. For values of $f(x)$ greater than 5, $f(x)$ may be represented by the

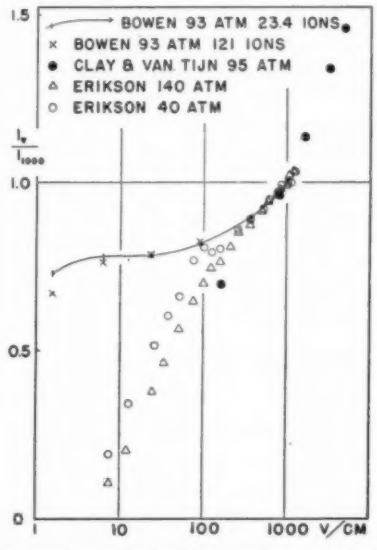

FIG. 1. Comparison of ionizations as a function of collecting field as obtained by various observers.

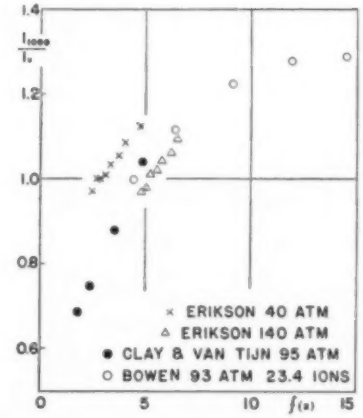

FIG. 2. Application of the Jaffé theory of columnar ionization using the graphical method suggested by Zanstra.

equation $f(x)=A-4.6$ log (collecting field/pressure) with an error of less than 1 percent. Consequently it is evident that the linearity cannot be improved by any reasonable shift of the constant A which is the only quantity not fully fixed by the Jaffé theory.

Another difficulty with the interpretation of these curves in terms of the Jaffé formula appears even in its application to the short linear sections of Clay and Van Tijn's curves. Thus they found from extrapolation by means of the Jaffé formula that the saturation currents, i.e., the number of ions originally formed, were less than half as great per atmosphere at 95 atmospheres as at one atmosphere. To explain this they assumed that at the lower pressure most of the secondary β-particles, that are the direct cause of the ionization, are ejected by the primary γ-rays from the walls of the vessel while at the higher pressure a large part of the β-rays are ejected from the air itself. The lower ionization per atmosphere at the higher pressure is then to be expected if the efficiency of the ejection of these secondary β-particles is greater from the walls, which are of relatively high atomic number, than from the air of low atomic number. However, Workman[7] found that the ionization was actually increased when the particles were ejected from an element of low atomic number such as carbon or aluminum rather than from steel or lead. Thus, if anything, more ions per atmosphere should be formed at the higher pressures.

All of these considerations show, therefore, that the observed variation of ion current with collecting field cannot be explained by the Jaffé formula for columnar recombination.

In conclusion the authors wish to emphasize again the importance of using very low rates of ionization in measurements at high pressure in order to eliminate ordinary volume recombination. When volume recombination is present the current collected is not proportional to the intensity of the ionizing radiation. Furthermore the curves of ion current *vs.* collecting field become a function not only of the intensity of ionization as discussed above but of the dimensions of the collecting chamber as well. Consequently the significance of these curves is limited chiefly to that of a calibration of the ionization chamber used. The limiting ionization current that can be used before volume recombination becomes appreciable depends of course on the pressure, collecting field and dimensions of the apparatus used. In general, however, for pressures over 25 atmospheres and collecting fields below a few hundred volts per cm the ionization current should be made as low as is feasible without having it masked by the residual ionization caused by cosmic rays and local radioactivity. Finally, measurements should be made at different rates of ionization to determine whether volume recombination has really been eliminated.

[7] E. J. Workman, Phys. Rev. **43**, 859 (1933).

Depolarization of Raman Lines and Structure of Chlorate, Bromate and Iodate Ions

S. T. SHEN, Y. T. YAO AND TA-YOU WU
Department of Physics, National University of Peking, Peking, China

The Raman spectra of chlorate ClO_3, bromate BrO_3 and iodate IO_3 in solutions are examined under high dispersion and the degrees of depolarization of the Raman lines measured. It is shown that the strong line at 930 cm^{-1} of ClO_3 and that at 800 cm^{-1} of IO_3 in solutions, which are regarded as single lines in the literature, are each really composed of two lines. The presence of four lines in each ion in the Raman effect, together with the depolarization measurement, and the infrared data, shows that these ions have pyramidal structure. The valence force constants of these ions are calculated from the present data according to the equations of Lechner.

INTRODUCTION

IN the literature[1] it is assumed that the chlorate ClO_3, bromate BrO_3 and iodate IO_3 ions have symmetric, plane structure like the carbonate ion CO_3. A symmetric, plane structure belongs to the symmetry class D_{3h} and possesses four vibrations: one totally symmetric vibration which is active in Raman effect but inactive in infrared absorption; one asymmetric with respect to the plane of the molecule and active in the infrared but inactive in Raman effect; and two doubly degenerate vibrations which are active in both Raman effect and the infrared. An examination of the Raman spectrum of ClO_3 ions in solution revealed, however, that in addition to the two lines at 479 cm^{-1} and 610 cm^{-1}, the strong line at 930 cm^{-1} has a wing on the high frequency side (measured from the exciting line), which suggests the presence of a weak line at 982 cm^{-1}. It is of some interest to investigate this further; for the presence of four Raman line would point to a pyramidal structure for the ion rather than a plane structure. A symmetric pyramidal model belongs to the symmetry class C_{3v} and possesses two totally symmetric vibrations ν_1, ν_2 in which the change of the electric moment is along the axis of the pyramid, and two doubly degenerate vibrations ν_3, ν_4 in which the change of the electric moment is perpendicular to the axis. All four vibrations are active in Raman effect. As the line 930 cm^{-1} of ClO_3 cannot be resolved from the wing even with high dispersion (12A per mm), and as the corresponding line in IO_3 (800 cm^{-1}) is only barely resolved into two lines at 779 and 826 cm^{-1}, it is thought desirable to study the depolarization of the Raman lines of ClO_3, BrO_3 and IO_3 with a view (i) to decide whether the line 930 cm^{-1} in ClO_3 and its wing are really two lines by observing their difference in the degrees of depolarization, and (ii) to decide between the plane model and the pyramidal model by comparing the observed spectra and the depolarizations with the selection and depolarization rules for the two models.

EXPERIMENTAL

The experimental method is of the conventional type. A mercury arc 14 cm long irradiated the Raman tube at a distance of 2 cm through two slits, each 0.8 cm wide, one near the arc and the other near the Raman tube. The scattered radiation was focused by a lens one meter from the tube and 43 cm from the slit of a three-prism Steinheil spectrograph with glass optics. Arrangement for exact parallelism of the exciting radiation was not attempted for it would necessitate unduly long exposures. The radiation was analyzed by a method due to Hanle.[2] A thick calcite crystal decomposed the radiation into two components; one with electric vector parallel to that of the exciting radiation and perpendicular to the length of the slit of the spectrograph, and a depolarized component with electric vector perpendicular to that of the exciting radiation and parallel to the length of the spectrograph. A second thin, wedge-shaped calcite crystal, cut

[1] C. Schaefer, F. Matossi and H. Aderhold, Zeits. f. Physik **65**, 289 (1930); C. Schaefer and F. Matossi, *Das Ultrarote Spektrum;* Cabannes, Ann. d. Physik **18**, 285 (1932), remarked in passing that in contrast with CO_3, ClO_3 has four Raman active frequencies but ν_3 could not be observed. We are indebted to Dr. H. C. Cheng for calling our attention to this remark. From x-ray studies and wave mechanical considerations, however, it is known that these ions ClO_3, BrO_3, IO_3 have pyramidal structure. See, for example, Slater, Phys. Rev. **38**, 325 (1931).

[2] W. Hanle, Zeits. f. Instrumentenk. **51**, 488 (1931).

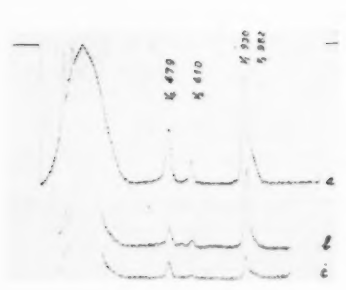

FIG. 1. ClO_3

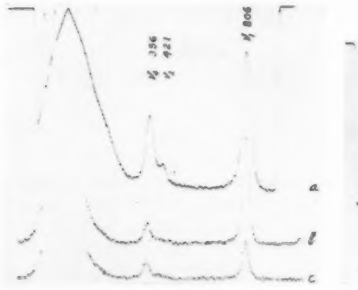

FIG. 2. BrO_3

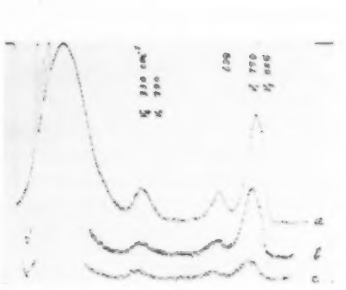

FIG. 3. IO_3

Raman spectra (a) without polarization, (b) polarized component, (c) depolarized component.

	ClO_3	BrO_3	IO_3
Concentration	10 N. $NaClO_3$	3 N. $NaBrO_3$	6.1 N. HIO_3
Slit width	0.06 mm	0.20 mm	0.06 mm
Exposure	250 hr.	230 hr.	210 hr.

with the optical axis in one face, was set with the axis at an angle of 45° with the slit to produce two images of depolarized light on the slit, so that difference in the loss of light due to reflections from the prism surfaces of the two components was eliminated. With this disposition, the two components were photographed simultaneously and exposures could be prolonged for the weak lines.

The comparison of the intensities of the two components of the Raman lines was made by the method of Thomson and Duffendack.[3] Intensity marks were put on the plate by means of a step-diaphragm. Intensity measurements were made on the microphotometer tracings of the line and the blackening-intensity curve at the position of the line.

In this study, excitation of the spectra was by means of the 4358 line. The jacket of the double-walled Raman tube contained a solution of sodium nitrite to filter off the line 4047 so as to eliminate the water band excited by it. This is necessary, for the broad water band falls in the region of the Raman lines of the ions excited by the line 4358 and would make intensity measurements very difficult. The Raman spectra of ClO_3, BrO_3 and IO_3 are represented in Figs. 1, 2, 3.

From Fig. 1, it is seen that the wing is more strongly depolarized than the line at 930 cm^{-1}, and it can be reasonably ascribed to a weak line with center at 980 cm^{-1}, though a decomposition of the intensity curve into two overlapping lines cannot be done entirely without arbitrariness. In BrO_3, the line at 421 cm^{-1} is observed for BrO_3 in solution for the first time. The strong line at 806 cm^{-1} is quite symmetrical, showing that the frequency ν_3 corresponding to the wing of the line 930 cm^{-1} in ClO_3 either is very close to $\nu_1 = 806$ cm^{-1} or is too weak to appear since the concentration of BrO_3 is low. In obtaining the curves *b* and *c*, the slit was opened up to 0.2 mm and the exposure was 210 hr. Even then the two components of ν_2 at 421 cm^{-1} were too weak to give an accurate value for the degree of depolarization. In IO_3,[4] the line at 330 cm^{-1} is broad and is due to two lines ν_4, ν_2 very close together. The line at 800 cm^{-1} is seen to be composed of two lines ν_1 and ν_3, the latter being more strongly depolarized than the former. Because of the overlapping of the two lines, an exact measurement of the intensity of the weak line ν_3 is impossible. However, by assuming a reasonable shape of the line ν_1 and by assuming that the half-width of the line is the same in the polarized and the depolarized components, a decomposition of the line into ν_1 and ν_3 may be performed

[3] K. B. Thomson and O. S. Duffendack, J. Opt. Soc. Am. **23**, 101 (1933).

[4] The line at 639 cm^{-1} is present in the Raman spectra of HIO_3 crystals but is not found in KIO_3 crystals (Kohlrausch, *Smekal-Raman Effekt*, S. 351). By varying the concentration of the HIO_3 in the solution, we found that the intensity of the line 639 cm^{-1} relative to the line 800 cm^{-1} decreases with decrease of concentration. These facts seem to show that the line 639 cm^{-1} is due to the undissociated molecule HIO_3. Quantitative measurement on the variation of the relative intensities of the line 639, 800, 330 with the concentration will be published elsewhere.

graphically. The degree of depolarization was then calculated by means of the log blackening-intensity curve. The values of ρ's for ν_3 of IO_3 and ClO_3 obtained in this manner must be regarded as qualitative.

The results of this study are summarized in Table I, which includes the infrared data[5] for comparison.

Discussion of Results

The presence of four lines in the Raman spectra of ClO_3, BrO_3 and IO_3 shows that they are inconsistent with a plane model, but fit in quite well with a pyramidal model. According to the polarization rule of Placzek,[6] the two symmetric vibrations ν_1 and ν_2 are partially depolarized and the values of the degrees of depolarization ρ should be less than 6/7; while the two degenerate vibrations ν_3 and ν_4 are completely depolarized and $\rho = 6/7$ for natural light. It is seen from Table I that wherever ρ has been measured, it agrees with the theory, except for ν_3 of IO_3 in which case ρ cannot be determined accurately because of the closeness of ν_3 to ν_1.

Further evidence[7] for the pyramidal structure is furnished by the infrared absorption curves of these ions in crystals. For the ClO_3 ion, Schaefer, Schubert, Matossi and Laski[5] observed three bands at 23μ (434 cm^{-1}), 16μ (624 cm^{-1}) and 10.04μ (994 cm^{-1}). At low dispersion, the band at 10μ shows an asymmetry consisting of a wing on the long wave-length side. A comparison between the infrared curve and the Raman line drawn on the same scale is given in Fig. 4. It is seen that the wing in the infrared absorption curve corresponds to a weak band due to the parallel vibration ν_1 which appears strongly in Raman effect, and the wing in the Raman curve corresponds to the perpendicular vibration ν_3 which is strong in infrared absorption.

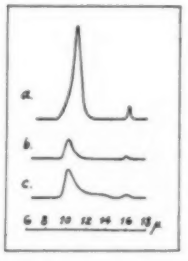

Fig. 4. (a) Raman lines of $NaClO_3$; (b) infrared curve of $NaClO_3$; (c) infrared curve of $KClO_3$.

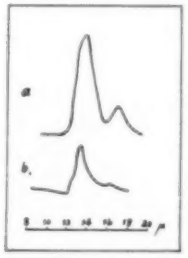

Fig. 5. (a) Raman lines of HIO_3; (b) infrared curve of KIO_3.

For BrO_3 two infrared bands at 23μ (434 cm^{-1}) and 12.2μ (820 cm^{-1}) are known, and a third at about 36μ (280 cm^{-1}) is obtained by extrapolation.[8] For IO_3, a band at 12.6μ (793 cm^{-1}) is observed, and one at 27μ (357 cm^{-1}) corresponding to ν_2 was obtained by extrapolation. A comparison between the infrared curve for the 12.6μ band and the Raman line at 800 cm^{-1} is given in Fig. 5.

Considering the low dispersion with which the infrared absorption curves were obtained, and

[5] C. Schaefer and M. Schubert, Zeits. f. Physik **7**, 309 (1921); C. Schaefer and Matossi, *Das Ultrarote Spektrum*, S. 328.

[6] Placzek, *Leipziger Vorträge*, 1931.

[7] An indirect reason against the plane model for these ions is that even if one neglects the presence of the line ν_2 in the Raman effect and proceeds to calculate the force constants of the ions, on the assumption of a plane model, using either the central force system of Dennison-Nielsen, Phys. Rev. **32**, 773 (1928), or the valence force system of Lechner, one is led to inconsistency in the equations giving the frequencies.

[8] C. Schaefer and F. Matossi, *Das Ultrarote Spektrum*, S. 328.

Table I. *The infrared and the Raman frequencies of ClO_3, BrO_3 and IO_3. The values in brackets are obtained by extrapolation only.[5] The values marked with an asterisk are taken from crystal data, Kohlrausch, "Smekal-Raman Effekt."*

	ν_1 ∥		ν_2 ∥		$\nu_3(2)$ ⊥		$\nu_4(2)$ ⊥	
	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared
ClO_3 ν	930 cm^{-1}	950 cm^{-1}	610 cm^{-1}	624 cm^{-1}	982 cm^{-1}	994 cm^{-1}	479 cm^{-1}	434 cm^{-1}
ρ	0.35		0.56		0.87		0.90	
BrO_3 ν	806	800	421	434	836*	820	356	(278)
ρ	0.38						0.89	
IO_3 ν	779	780	390*	(357)	826	793	330	
ρ	0.43				0.67		0.81	

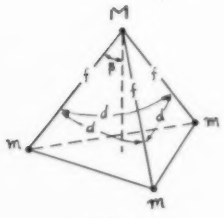

FIG. 6.

remembering that the long wave-length bands[8] were obtained by the Reststrahlen method of which the accuracy is very low, and that the infrared frequencies and the Raman frequencies were obtained for the ions in crystals and in solutions respectively, one feels that the agreement between the Raman data and the infrared data is as good as one would expect. It is desirable to examine the 10μ band of ClO_3 and the 12.6μ band of IO_3 in the infrared with higher dispersion, and to determine more accurately the positions of the long wave-length bands of these ions.

Assuming a pyramidal model, one can calculate the force constants of these ions. On the basis of a valence force system, Lechner[9] obtained the following equations for the four frequencies $\nu_i=\sqrt{\lambda_i}/2\pi$:

$$\lambda_1\lambda_2=(f/m)(6d/m)2p\cos^2\beta/(1+3\cos^2\beta),$$
$$\lambda_1+\lambda_2=(f/m)[1+(p-1)\cos^2\beta]+(6d/m)[p-(p-1)\cos^2\beta]2\cos^2\beta/(1+3\cos^2\beta),$$
$$4\lambda_3\lambda_4=(f/m)(6d/m)[p+(2-p)\cos^2\beta]2/(1+3\cos^2\beta),$$
$$2(\lambda_3+\lambda_4)=(f/m)[p+1-(p-1)\cos^2\beta]+(6d/m)[1+(p-1)(1-\cos^2\beta)^2/2(1+\cos^2\beta)](1+\cos^2\beta)/(1+3\cos^3\beta),$$

where $p=(3m+M)/M$, and ν_1, ν_2 are the single frequencies and ν_3, ν_4 are the doubly degenerate frequencies.

TABLE II. *Constants of the CLO_3, BrO_3, IO_3 ions.*

	$f\times10^{-5}$	$6d\times10^{-5}$	β
ClO_3	5.55	6.42	54°
BrO_3	5.25	3.52	53.5°
IO_3	5.35	3.19	53.3°

By substituting the observed frequencies in these equations and so adjusting the values of the constants f, d and β that the two sides of the equations are closest to each other, we obtain the values of f, d, β for the ions given in Table II.

In conclusion, we wish to acknowledge our indebtedness to Dr. Ny Tzi-Zé, of the Institute of Physics, Peiping Academy, for the use of the microphotometer.

[8] F. Lechner, Graz Dissertation, 1933; Monatshefte f. Chemie **61**, 385 (1932).

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The $^1\Sigma^*-{}^1\Sigma$ Band System of Ionized Cadmium Deuteride

R. V. ZUMSTEIN, J. W. GABEL AND R. E. McKAY
Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio

(Received November 9, 1936)

The $^1\Sigma^*-\Sigma$ bands have been photographed with a dispersion of about 1.3A/mm. Eight bands of the system, between $\lambda2630$ and $\lambda2280$ were analyzed. The isotopic coefficient ρ agrees with the value obtained from atomic weights. The electronic isotope displacement relative to Cd^+H appears to be 4.4 cm^{-1}. However, this value is somewhat uncertain as only three vibrational levels of the upper state and four of the lower state are available. The lines did not show a fine structure from the cadmium isotopes.

THE band spectrum of the ionized cadmium hydride molecule has been investigated by Svensson and Tyrén[1] who give references to previous work. We have studied the similar spectrum obtained by substituting deuterium for hydrogen, thus providing additional experimental evidence concerning the problem of the electronic isotope effect.

EXPERIMENTAL

The spectrum was excited in an end-on discharge tube of fused quartz. The length of the

[1] E. Svensson and F. Tyrén, Zeits. f. Physik **85**, 257 (1933).

TABLE I. *Wave numbers of the ionized cadmium deuteride bands.*

J	R	P
0−0 band		
4	42758.4*	42715.4
5	758.4*	704.0
6	755.1	691.8
7	751.5	678.8
8	747.0	664.0
9	741.0	648.8
10	734.2	632.1
11	726.1	615.0
12	716.5	595.6
13	705.6	575.5
14	693.6	554.7
15	680.9	531.7
16	666.5	508.4
17	650.3	483.7
18	633.8	457.7
19	615.9	430.5
20	596.4	401.8
21	575.5	373.1
22	554.8	342.2
23	531.7	310.2
24	508.4	277.5
25	483.6	244.0
26		209.3
27		172.7
28		135.0
0−1 band		
3		41503.0
4	41535.3*	491.9
5	535.3*	481.6
6	533.7	470.6
7	531.1	458.8
8	527.5	444.8
9	522.8	430.5
10	517.4	415.3
11	510.7	399.6
12	502.7	382.2
13	494.0	363.9
14	484.0	344.5

J	R	P
0−1 band (*cont'd*)		
15	472.6	324.5
16	461.1	302.9
17	447.2	280.2
18	433.3	256.9
19	417.9	231.5
20	401.3	206.1
21	383.3	180.1
22	363.9	152.2
23	344.5	121.3
24	324.5	093.8
25	302.9	064.1
26	280.2	032.2
27	256.9	000.1
28		40964.9
29		930.3
0−2 band		
2		40322.6
3		314.6
4		305.8
5	40349.9*	296.8
6	349.9*	286.2
7	349.9*	276.3
8	345.5	263.5
9	342.1	250.0
10	337.2	235.9
11	330.0	221.4
12	326.3	205.3
13	319.2	188.5
14	311.2	171.5
15	301.9	152.6
16	291.7	132.0
17	281.1	113.7
18	269.1	091.9
19	256.8	070.2
20	242.6	047.5
21	228.3	40024.2
22	212.0	39998.7
23	195.9	973.0

J	R	P
0−2 band (*cont'd*)		
24	178.3	947.5
25	159.3	
26	140.7	
27	120.1	
1−0 band		
4	43636.1*	
5	636.1*	43582.7
6	632.9	570.5
7	628.5	556.1
8	623.4	541.8
9	617.4	526.2
10	609.8	509.0
11	600.6	490.6
12	590.3	470.9
13	578.9	449.9
14	566.1	425.5
15	552.1	405.0
16	537.0	380.1
17	521.1	354.6
18	502.1	327.3
19	483.2	299.9
20	462.4	269.9
21	441.7	239.3
22	417.6	208.4
23	393.9	175.1
24	369.5	140.7
25		105.4
1−2 band		
4	41231.5*	41186.4
5	231.5*	177.4
6	229.4	165.8
7	227.5	154.7
8	224.3	143.0
9	220.6	129.1
10	215.2	114.9
11	209.5	098.9
12	200.8	082.5

J	R	P
1−2 band (*cont'd*)		
13	193.9	064.1
14	184.4	046.6
15	174.8	028.0
16	164.3	41007.0
17	149.1	40985.7
18	139.3	964.9
19	121.3	941.2
20	109.6	916.4
21	093.8	896.2
22	077.0	
23	058.5	
24	041.2	
1−3 band		
1		40062.3
2		056.3
3		047.5
4		039.8
5		030.3
6	40083.1*	020.7
7	083.1*	009.7
8	081.2	39998.7
9	077.1	986.3
10	073.7	973.0
11	068.4	959.1
12	063.4	944.5
13	057.3	928.8
14	050.2	912.5
15	042.0	894.1
16	033.7	876.1
17	024.2	858.2
18	012.9	839.0
19	40001.7	818.0
20	39989.1	797.6
21	976.0	775.4
22	962.8	753.0
23	947.5	730.1
24	932.2	704.4
25	915.9	

J	R	P
2−2 band		
3		42068.5
4		059.6
5		049.3
6		038.4
7		026.6
8		42013.4
9		41999.2
10		984.2
11		968.2
12		950.6
13		932.2
14		913.2
15		893.6
16		872.2
17		849.7
18		826.9
2−4 band		
2		39818.0
3		811.1
4		803.3
5		794.9
6	39846.1*	784.9
7	846.1*	775.4
8	846.1*	764.0
9	842.9	753.0
10	839.0	740.2
11	836.4	730.1
12	831.3	714.1
13	825.8	699.5
14	819.8	684.5
15	813.2	668.4
16	804.7	651.2
17	797.6	634.4
18	786.9	615.6
19	777.6	596.7
20	765.0	
21	755.0	
22	742.0	

* Band heads.

tube was 20 cm and its diameter 1 cm. Small pieces of cadmium metal were scattered along the fused quartz tube and the latter placed inside a water cooling jacket made of Pyrex glass. Since the water did not strike the quartz directly we obtained sufficient temperature to evaporate the cadmium. The heavy hydrogen, prepared by the reaction between calcium metal and 99.5 percent deuterium oxide, slowly entered the tube through a needle valve. The spectrum was excited by a 2300 volt direct current generator with sufficient series resistance to limit the current to about 2 amperes. After a few minutes operation we always observed a rapid clean up of the deuterium. This seemed to be very important when a spectrum free from the light hydrogen is desired. By this method plates were obtained showing no trace of the light hydrogen. The spectrum was photographed with a large Hilger quartz spectrograph having a dispersion of about 1.3A per mm. This is about the same as the dispersion of a 30,000 lines/inch, 21-foot grating when used in the first order.

ANALYSIS

The measurements of the individual wave numbers of the band lines are given in Table I directly as measured with a Société Génevoise

TABLE II. *Null lines.*

v' \ v''	0	1	2	3	4
0	42746.9	41523.2	40334.8		
1	43626.6		41215.7	40068.6	
2			42089.5		39829.6

TABLE III. *Constants from the rotational structure.*

v	B_v'	$-D_v'$	B_v''	$-D_v''$
0	2.438	0.000076	3.052	0.000058
1	2.412	0.000084	2.966	0.000060
2	2.380	0.000092	2.903	0.000079
3			2.833	0.000086
4			2.777	0.000108

TABLE IV. *Summary of constants.*

	$^1\Sigma$ lower state	$^1\Sigma^*$ upper state
ω_e	1262.5	887.2
$x_e\omega_e$	19.01	3.44
T_e	0	42930.6
B_e	3.075	2.451
α_e	0.0682	0.027
D_e	−0.000048	−0.000072

comparator. The band heads are indicated by starred lines in the R branch. Within any band the measurements should have an average accuracy of about 0.4 cm^{-1}. In addition to these errors of setting the microscope, the band as a whole may be shifted relative to the comparison spectrum by about 0.5 cm^{-1}. In the 0−0 and 0−1 bands, which are favorably situated, the returning R branch almost coincides with the P branch. This entirely hides the null line and other faint lines nearby. Fortunately the 0−2, 1−3 and 2−4 sequence presented no such overlapping. The null lines were close to the band heads. The continuous spectrum of the deuterium molecule was always present and this also helped to hide faint lines. Thus the assignment of J values depended largely on the combination differences, $R(J)-P(J)$ and $R(J-1)-P(J+1)$.

TABLE V. *Isotope ratios Cd$^+$D : Cd$^+$H.*

	$^1\Sigma$	$^1\Sigma^*$
$(Be^i/Be)^{\frac{1}{2}}$	0.7117	0.7108
ω_e^i/ω_e	0.7113	0.7086
$(\mu/\mu_i)^{\frac{1}{2}}$	0.7105	

TABLE VI. *Other band heads observed but not analyzed.*

Designation	ν
1–4	38976.9
2–5	780.0
3–6	616.1
4–7	482.6
5–8	382.4
6–9	315.7
7–10	288.2
8–11	271.6
9–12	261.2

In this analysis we have used the energy expressions given by Mulliken.[2] Wherever possible the least squares method of Birge and Shea[3] was used in performing the calculations. The B and D constants were also determined by the graphical method described by Bengtsson Knave.[4] It was always found that the individual lines of the P branch could be represented by a least squares parabola within the limit of error of the observations. The results of the analysis are given in Tables II, III and IV. The system as a whole checks with the established isotope theory as is shown by Table V. If we take T_e for Cd$^+$H as 42,935 we find an electronic isotope displacement for Cd$^+$D of 4.4 cm^{-1}. It seems to us that more bands of the system should be analyzed with greater dispersion before this last number can be regarded as certain. A fine structure of the lines due to the cadmium isotopes was not observed.

[2] R. S. Mulliken, Rev. Mod. Phys. **2**, 66 (1930).
[3] R. T. Birge and J. D. Shea, University of California Pub. in Math. **2**, 93 (1927).
[4] E. Bengtsson Knave, Nova. Acta. Reg. Soc. Upsaliensis Ser. IV, Vol. 8, No. 4, p. 12 (1932).

Interferometer Wave-Lengths of Certain Lines in the Secondary Spectrum of D_2 and HD

NORTON A. KENT AND REGINALD G. LACOUNT
Boston University, Boston, Massachusetts

(Received December 11, 1936)

Interferometer determinations of the wave-lengths of thirty-eight lines in the spectra of deuterium and HD in the region λ4860 to λ5800 have been made by a crossed etalon and Littrow spectrograph. The measurements show a mean probable error of 0.0003A.

INTRODUCTION

WITH a spectrum as rich in lines as the secondary spectrum of hydrogen, interferometric determinations of the wave-lengths of certain lines distributed throughout the spectrum are extremely valuable as tertiary standards.

The present paper covers the region from λ4860 to λ5800 with D_2 and HD.

APPARATUS

The Pyrex glass discharge tube was built in U form with platinum terminals at each end, the capillary being of 7 mm internal diameter and 36 cm length, coated inside with platinum bright to enhance the molecular spectrum. The tube was mounted in a tank in which a continuous flow of water was maintained. A 5 kw transformer supplied to the terminals of the tube a 190 ma current (current density 490 ma/cm²) at 14,000 volts. A flask of deuterium gas[1] was connected with the vacuum system through three stopcocks, thus rendering the gas flow controllable.

The general arrangement of apparatus is shown in Fig. 1.

The auxiliary dispersing Littrow spectrograph has a lens of 6-inch aperture and 30-foot focal length with an Anderson plane grating of 15,000 lines to the inch and a ruled space of 9.7×12.9 cm. The first order was used, the dispersion being about 1.8A per mm. The etalon was aluminum coated and had a separation of about 10 mm.

When the spectrograph slit was open, the image of a diaphragm (not shown in Fig. 1), placed as near the etalon as possible and on the side away from the source, formed upon the grating by the concave mirror N, nearly covered the ruled surface of the grating.

PROCEDURE

The spectrum of a standard Pfund arc was photographed on each plate, the arc being exposed for about one minute every half-hour during the tube exposure which in all cases was nine hours. The wave-lengths recommended by the International Astronomical Union were used as standards.[2]

The D_2 spectrum was photographed first by allowing a small quantity of gas to pass from the reservoir into the tube and then isolating the tube by a stopcock at each end. A pressure of 0.3 mm was found to produce the best spectrum.

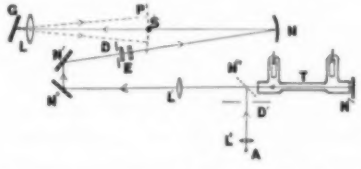

FIG. 1. General arrangement of optical train. Not drawn to scale.

G—plane grating.
L—six-inch lens of 30-foot focal length.
S—slit of Littrow spectrograph.
P—photographic plate (below slit).
N—concave mirror of 97.3 cm focal length.
E—etalon.
D—diaphragm with opening approximately 1 cm square.
N', *N''*—plane mirrors.
L'—lens forming image of capillary of tube *T* upon *D* when *N''''* is removed.
N''''—plane mirror used for throwing light from arc upon *D*, light from tube being then intercepted.
T—vacuum tube.
N'''''—plane mirror to increase brilliancy of source.
D'—diaphragm with 1 cm vertical aperture to cut out all but central portion of arc.
L''—short focus lens giving 10-fold magnification of source *A* upon *D'*.
A—Pfund arc, 13 to 15 mm in length.
All mirrors are aluminum coated.
All lenses are achromats.
Mirrors *N'* and *N''* were necessary because of the narrowness of the room.

[1] Purchased from Professor Hugh S. Taylor of Princeton University.

[2] Transactions of International Astronomical Union III, 86 (1928).

TABLE I. *Wave-lengths, in angstroms, of deuterium and HD.*

Deuterium				HD	
Intensity	Wave-length	Intensity	Wave-length	Intensity	Wave-length
0	4875.671	0^1	5460.467	0	4900.298
0^3	4913.497	0	5473.457	0	4988.770
0^3	4963.200	0	5481.942	1	4990.692
0^4	4965.643	0^1	5488.596	0	4991.654
0^4	4968.567	1	5609.285	0^1	5209.520
0^3	5024.446	0	5631.729	0	5362.868
0^2	5070.930	0	5639.085	0	5381.903
0^1	5100.014	0	5664.392	1	5477.495
0^3	5204.451	1	5690.228	0	5525.040
0^4	5254.361	1	5702.698	1	5563.479
0^4	5259.619	2	5715.583	1	5582.449
0^3	5294.952	1	5796.627	0	5589.146
				0	5624.862
				0^1	5667.768

To obtain the HD spectrum, hydrogen, electrolytically prepared and dried by passing through tubes of calcium chloride and dessichlora, was passed into the tube containing deuterium and the pressure pumped down to the correct value. The spectrum was observed visually by means of a direct vision spectroscope, this serving as a guide to the appropriate mixture of hydrogen and deuterium. Eastman spectroscopic plates I–D were used throughout.

RESULTS

The method of reduction of wave-lengths was that employed at Mount Wilson,[3] and was based on the familiar relations; $2t=p\lambda$, and $E=D^2/(D_k^2-D_{k-1}^2)$ where t is the thickness of the etalon; p the order of interference at the center of the rings; λ the wave-length; E the fractional part of the order of interference; D the diameter of a bright ring; and k the number of the ring, counting from the center.

[3] Babcock and St. John, Astrophys. J. **53**, 260 (1921).

Dr. Dieke of Johns Hopkins University kindly provided most of the preliminary wave-lengths forming the basis of the measurements. These were correct to 0.01A; hence only one thickness of etalon was necessary.

The wave-lengths listed in Table I are the means of measurements on five plates for D_2 and five for HD. For only two of the twenty-five D_2 lines measured is the probable error as great as 0.0006, and for sixteen it is not greater than 0.0003, the average being 0.0003A. Of the fourteen HD lines the probable error for one is 0.0005, and for ten it is 0.0003 or less, the average being 0.0003A.

The intensities listed were estimated by eye, O^4 indicating that the line is just seen on the plate, O being the average intensity and 3 that of the strongest lines.

The major part of the work was done by the junior writer of this paper and was carried out in the Rumford Committee room in the Eastman Spectroscopic Laboratory of the Massachusetts Institute of Technology. This entire building is insulated from vibration and thermostatically controlled, and is therefore well suited for long exposures.

The writers wish to acknowledge their indebtedness to the Institute for the splendid facilities placed at their disposal, and to Drs. Harrison and Boyce especially for their valuable suggestions.

We are also indebted to Mr. Babcock of Mt. Wilson Observatory for his helpful advice, to Professor Wood of Johns Hopkins for the loan of the grating, and to Dr. Dieke for furnishing some of the necessary preliminary wave-lengths.

A grant from the Rumford Committee of the American Academy of Arts and Sciences to the senior writer made this research possible.

The Zeeman Effect of N II

J. B. GREEN AND H. N. MAXWELL*
Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio
(Received November 26, 1936)

The Zeeman effect of N II has been studied at field strengths of about 36,000 gauss. By using helium as residual gas with a small nitrogen impurity, the spectrum has been strongly excited, especially in the visible region. Edlén's corrections to Freeman's classification have been verified. Except in a few important cases, g values are LS within experimental error. The exceptions are considered in detail.

THE spectrum of N II was first well classified by Fowler and Freeman[1] and later extended by Freeman[2] who found quintet combinations in addition to the singlets and triplets and singlet-triplet intercombinations found by Fowler and Freeman. In the meantime, some work by Pretty[3] had disclosed some new singlet levels, but Edlén[4] has shown that Pretty's interpretation of his results is probably incorrect. Thus, the $3p\,{}^1P_1$ and $3p\,{}^1D_2$ assigned by Freeman were interchanged by Edlén.

Studies of the Zeeman effect of N II indicate that Edlén's interpretation is the correct one. The Zeeman effect of N II was first studied by Croze[5] over twenty years ago. The patterns were, in general, unresolved, and were therefore of very little use in helping to classify the spectrum or to study perturbations in the classified spectrum. The present investigation was carried out along with other work in our systematic study of the Zeeman effect.

The atomic spectra of N are not usually excited with any great intensity in the spark discharge in air or in partial vacuum. But when a discharge takes place between metal electrodes in an atmosphere of helium with a small percentage of nitrogen, the spectrum of N II is very strongly excited. This would indicate that the N_2 molecule when ionized by electron impact dissociates into two N^+ ions. In the present investigation, the discharge took place between gold or gold and copper electrodes. The upper electrode was a piece of No. 20 gold wire held in a brass rod and the lower electrode was a gold or copper wire wrapped on a brass disk which rotated about an axis so that its periphery was at the center of the magnetic field. The interaction of the current in the upper electrode and the magnetic field causes the arc to be intermittent, the greater the current the longer the period during which the arc remains lit.

The exposures varied from a few hours up to 48 hours, and the arc current averaged about 0.7 ampere. Most of the measurements were made from an exposure between gold and copper electrodes which lasted about 38 hours and was spread over a period of about four days. The temperature of the grating was carefully controlled by an ether thermostat and no effects due to changing temperature could be observed on some of the finely resolved patterns of copper and gold.

About fifty lines in the spectrum of N II were measured in a field of about 36,000 gauss and the results are tabulated in Table I. Typical Zeeman patterns are shown in Fig. 1.

The lines are arranged in multiplets and the g values have been calculated using the resolved patterns first, and then using the g values thus obtained from the same multiplet (wherever

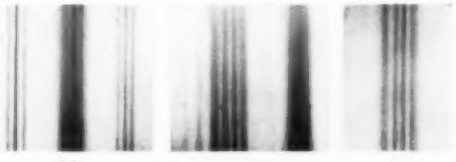

FIG. 1. Typical Zeeman patterns of N II. (a) λ5045, (b) λλ5010.6 and 5007.3, (c) λ4994.3.

* Instructor in mathematics, Hood College, Frederick, Maryland.
[1] Fowler and Freeman, Proc. Roy. Soc. **A114**, 662 (1927).
[2] Freeman, Proc. Roy. Soc. **A124**, 654 (1929).
[3] Pretty, Proc. Phys. Soc. London **41**, 442 (1929).
[4] Edlén, Nov. Acta Reg. Soc. Sci. Upsala, Sev. **IV**, 9, No. 6.
[5] Croze, Ann. de physique **1**, 35 (1914).

TABLE I. *Zeeman pattern and g values for lines in the spectrum of N II.*

λ	CLASSIFICATION[4]	ZEEMAN PATTERN	g_1	g_2
3994.995	$3s\ ^1P_1 - 3p\ ^1D_2$	(0) 0.980	1.052	1.004
4432.71	$3d\ ^3P_2 - 4f\ ^3D_3$	(0) 1.096	1.50	1.30
4447.035	$3p\ ^1P_1 - 3d\ ^1D_2$	(0) 0.976	1.005	0.986
4530.37	$3d\ ^1F_3 - 4f\ ^1G_4$?	(0) 1.017	—	—
4601.490	$3s\ ^3P_1 - 3p\ ^3P_2$	(0) 1.514	1.457	1.495
4607.167	$^3P_0 - {}^3P_1$	(0) 1.530	—	1.530
4613.884	$^3P_1 - {}^3P_1$	(0) 1.500	1.465	1.535
4621.405	$^3P_1 - {}^3P_0$	(0) 1.457	1.457	—
4630.551	$^3P_2 - {}^3P_2$	(0) 1.502	1.509	1.495
4643.106	$^3P_2 - {}^3P_1$	(0) 1.475	1.493	1.530
4779.710	$3p\ ^3D_1 - 3d\ ^3D_1$	(0) 0.495	0.495	0.495
4778.126	$^3D_2 - {}^3D_2$	(0) 1.140	1.167	1.113
4803.272	$^3D_3 - {}^3D_3$	(0) 1.333	1.333	1.333
4895.20	$2p'\ ^1D_2 - 3p\ ^1P_1$	(0) 0.971	0.985	1.013
4987.377	$3p\ ^3S_1 - 3d\ ^3P_0$	(0) 2.018	2.018	—
4994.358	$- {}^3P_1$	(0.495) 1.505 2.009	2.010	1.505
5007.316	$- {}^3P_2$	(0) (0.490) 1.012 1.514 2.00	2.008	1.514
5001.469	$3p\ ^3D_2 - 3d\ ^3F_3$	(0) 0.976	1.166	1.071
5005.140	$^3D_3 - {}^3F_4$	(0) 1.125	1.333	1.250
5025.665	$^3D_3 - {}^3F_3$	(–) (0.747)—	1.333	1.086
5012.026	$3s'\ ^5P_3 - 3p'\ ^5P_3$	(0) 1.664	1.664	1.664
5002.692	$3s\ ^3P_0 - 3p\ ^3S_1$	(0) 2.022	—	2.022
5010.620	$^3P_1$	(–) 1.460 2.016	1.460	2.016
5045.098	$^3P_2$	(0) (0.515) 1.000 1.495 —	1.505	2.015
5175.89	$3p'\ ^5D_2 - 3d'\ ^5F_4$	(0) 1.087	—	—
5179.50	$^5D_4 - {}^5F_5$	(0) 1.073	—	—
5452.12	$3p\ ^3P_0 - 3d\ ^3P_1$	(0) 1.478	—	1.478
5454.26	$^3P_1 - {}^3P_0$	(0) 1.528	1.528	—
5462.62	$^3P_1 - {}^3P_1$	(0) 1.508	1.533	1.483
5478.13	$^3P_1 - {}^3P_2$	(0) 1.486	1.528	1.500
5480.10	$^3P_2 - {}^3P_1$	(0) 1.502	1.495	1.481
5495.70	$^3P_2 - {}^3P_2$	(0) 1.496	1.492	1.500
5535.39	$3s'\ ^5P_{2,1} - 3p'\ ^5D_{4,1}$	(0) 1.079	—	—
5666.64	$3s\ ^3P_1 - 3p\ ^3D_2$	(0) (0.282) 0.888 1.167 —	1.448	1.167
5676.02	$^3P_0 - {}^3D_1$	(0) 0.487	—	.487
5679.56	$^3P_2 - {}^3D_3$	(0) 1.104	1.532	1.319
5686.21	$^3P_1 - {}^3D_1$	0.501 (0.935) 1.444	1.442	.501
5747.29	$3s\ ^1P_1 - 3p\ ^3D_2$	(0) 1.216	1.056	1.163
5927.82	$3p\ ^3P_0 - 3d\ ^3D_1$	(0) 0.493	—	.493
5931.79	$^3P_1 - {}^3D_2$	(0) 0.910	1.53	1.115
5941.67	$^3P_2 - {}^3D_3$	(0) 1.143	1.509	1.325
6167.82	$3d\ ^1P_1 - 4p\ ^1S_0$; $3d\ ^3F_4 - 4p\ ^3D_3$	(0) 1.146	1.250	1.319
6170.16	$^3F_2 - {}^3D_1$	(0) 0.777	0.682	0.50
6173.40	$^3F_3 - {}^3D_2$	(0) 0.913 ?	1.086	1.259
6284.30	$3p\ ^1D_2 - 3d\ ^1P_1$	(0) 0.987	1.000	1.026
6379.63	$3s\ ^3P_1 - 3p\ ^1P_1$	(0.450) —	1.455	1.005
6482.07	$3s\ ^1P_1 - 3p\ ^1P_1$	(0) 1.026	1.047	1.005

TABLE II. *Configurations $1s^22s^22p3s$.*

TERM	g(obs)	g(*LS*)	g (Houston)[7]	
$3s\ ^3P_2$	1.502	1.500	1.500	
$3s\ ^1P_1$	1.051	1.000	1.055	
$^3P_1$	1.455	1.500	1.445	
	2.506	2.500	2.500	Σg
$3s\ ^3P_0$	—	—	—	

TABLE III. *Configuration $1s^22s^22p3p$.*

TERM	g(obs)	g(*LS*)	
$3p\ ^1S_0$	—	—	
$^3P_0$	—	—	
$3p\ ^1P_1$	1.005	1.000	
$^3S_1$	2.015	2.000	
$^3P_1$	1.530	1.500	
$^3D_1$	0.494	0.500	
	5.044	5.000	Σg
$3p\ ^1D_2$	1.002	1.000	
$^3P_2$	1.497	1.500	
$^3D_2$	1.166	1.167	
	3.665	3.667	Σg
$3p\ ^3D_3$	1.330	1.333	

TABLE IV. *Configuration $1s^22s^22p3d$.*

TERM	g(obs)	g(*LS*)	
$3d\ ^3P_0$	—	—	
$3d\ ^1P_1$	1.026	1.000	
$^3P_1$	1.487	1.500	
$^3D_1$	0.494	0.500	
	3.007	3.000	Σg
$3d\ ^1D_2$	0.986	1.000	
$^3P_2$	1.504	1.500	
$^3D_2$	1.114	1.167	
$^3F_2$	—	0.667	
		4.333	Σg
$3d\ ^1F_3$	—	1.000	
$^3D_3$	1.329	1.333	
$^3F_3$	1.079	1.083	
		3.417	Σg
$3d\ ^3F_4$	1.250	1.250	

possible), the *g* values from the unresolved patterns were determined.[6]

The *g* values thus obtained are summarized in Tables II, III, IV. The results shown are weighted averages.

[6] See e.g., Shenstone and Blair, Phil. Mag. **8**, 765 (1929).

In our previous work, we have stated that the *g* values obtained have an accuracy of about one-half percent. In the present work, due to the lack of sharpness of the lines, we must increase the limit of error, and suggest that this accuracy is not better than one percent. An inspection of the

tables shows that wherever it is possible to give g sums, that they show an accuracy of considerably better than 1 percent, but we believe this result to be entirely fortuitous.

The configuration $1s^2 2s^2 2p3s$ is compared with Houston's[7] calculations for this configuration and the two levels with $j=1$ show considerable deviation from LS coupling and gratifying agreement between theory and observation.

Of particular interest in connection with the configuration $1s^2 2s^2 2p3p$, is the line λ6379, which has a pattern belonging definitely to a transition in which $\Delta j=0$, thus showing that Fowler and Freeman's and Pretty's designation of the level $3p\,{}^1P_1$ (called by them $3p\,{}^1D_2$) is incorrect, as pointed out by Edlén, on the basis of selection rules.

The configurations $1s^2 2s^2 2p3p$ and $1s^2 2s^2 2p3d$ show a large perturbation of the middle term of the middle triplet. $3p\,{}^3P_1$ has a g value of 1.530 and $3d\,{}^3D_2$ has a g value of 1.114, the LS g values being 1.500 and 1.167, respectively. Both of these results are too far different from the LS values to be accounted for on the basis of experimental error. No other levels of the configurations are close enough to produce perturbations of so large a magnitude. Nevertheless there are perturbations in both cases, as is evidenced by the fact that the $3p\,{}^3P$ separations are in the ratio 1.65 : 1 instead of 2 : 1; and the $3d\,{}^3D$ separations are in the ratio 2.52 : 2 instead of 3 : 2 for LS coupling. In addition to this, it has been pointed out by Condon and Shortley[8] that the intermultiplet separations are also considerably different from the LS values for the $2p$ and $3p$ configuration for the whole isoelectronic sequence C I, N II, O III, being in the ratio of 2.27 : 2 instead of 3 : 2 for $P-D/D-S$. They attribute this to interaction between the $2p$ and $3p$ configurations. There could also be configuration interaction between either of these configurations and the configuration $1s^2 2p^4$; and between the $3d$ configuration and $1s^2 2s 2p^3$. Perturbations of this type are electrostatic, however, and their effects on g values would come as a result of their spoiling the electrostatic parameters which would in turn perturb the LS ratios and thus secondarily affect the g values.

[7] Houston, Phys. Rev. **33**, 297 (1929).

[8] Condon and Shortley, *Theory of Atomic Spectra* (Cambridge University Press, 1935).

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The Refractive Index of Water for Electromagnetic Waves Eight to Twenty-Four Centimeters in Length

THOMAS T. GOLDSMITH, JR.
Cornell University, Ithaca, New York

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Wave-lengths were measured in air and water for continuous waves produced by magnetron and positive grid oscillators. Although high in absolute value, the index of refraction thus determined shows a decrease with increasing frequency, indicating a start of the drop toward the infrared value.

INTRODUCTION

EARLY attempts[1, 2] with electromagnetic waves from spark sources have been made to detect experimentally the beginning of the dispersion region where the index of refraction of water drops from the long wave value of $\mu=\sqrt{\epsilon}=9$ toward the infrared value of $\mu=1.33$. This paper reports an investigation in the interval of wave-lengths from eight to twenty-four centimeters, making use of the improved stability obtainable with the magnetron and positive grid oscillators as sources of short electromagnetic waves.

Debye[3] and Bernal and Fowler[4] give some theoretical discussion indicating probable dispersion in this region.

[1] Nichols and Tear, Nat. Acad. of Sci. Proc. **9**, 211 (1923).

[2] Glagolewa-Arkadiewa, Nature **113**, 640 (1924).

[3] Debye, *Polar Molecules* (Chemical Catalog Company, 1929), p. 85.

[4] Bernal and Fowler, J. Chem. Phys. **1**, 515 (1933).

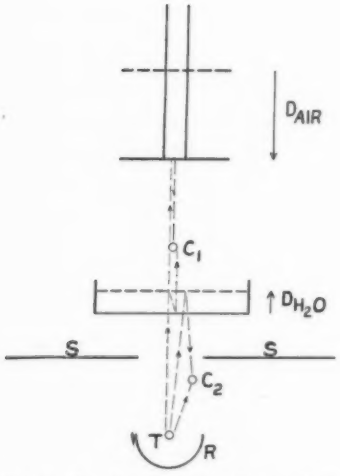

FIG. 1. Wave-length measuring system.

EXPERIMENTAL METHOD

The wave-length measuring system, Fig. 1, is a modification of that described by Miesowicz.[5] Polarized radiation from the transmitting antenna T, reinforced by the reflector R, passes between the screens S and up through the tank of water, reaching the crystal detectors C_1 and C_2 over the indicated paths. It can be seen that each crystal receives two beams of energy, one of which has been retarded over the other by passage through two thicknesses of the water. By interference, the energy received at either crystal goes through maxima and minima as the water thickness is varied. The spacing between successive maxima or minima of this interference curve, plotting current from the crystal detector against the water thickness, is one-half the wave-length of the waves in water. Similarly, the movable reflector shown above the crystal C_1 produces interference from which the wave-length in air can be determined. Fig. 2 shows several typical curves for both air and water.

The transmitters used are similar in general to those described adequately in the literature[6–11] except that the magnetron tubes were designed and built to be useful over a range of an octave for each tube. The positive grid tubes were of conventional design.

A more elaborate interferometer system, designed to measure the absorption coefficient as well as the index of refraction, was built and tried but proved unsatisfactory because of the intense diffracted energy which came around the mirrors employed in the interferometer. Its mirrors were 12 by 16 inches in size. Satisfactory results might be obtained with a much larger system, though a greater beam intensity would be required.

The curves with C_2 proved more satisfactory than those with C_1, because the interference with C_2 is superposed upon a straight zero line, while the interference with C_1 is superposed on the absorption curve for the water, making the peaks more difficult to locate. This can be seen by inspection of the water curves of Fig. 2. All curves were interpreted by taking as many independent peak-to-peak and trough-to-trough intervals as possible. Several curves were taken at each wave-length.

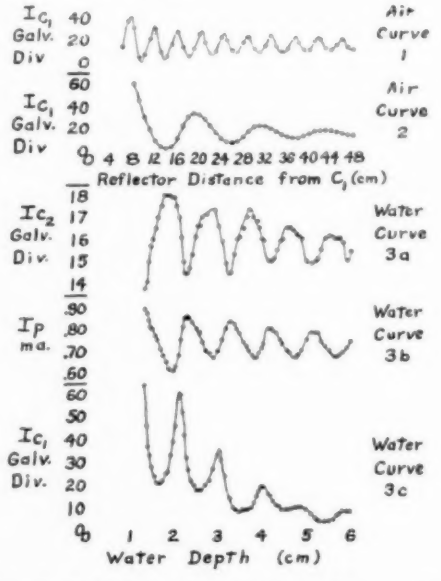

FIG. 2. Typical air and water interference curves. Curve 1. Air. $\lambda_0 = 8.53$ cm. Curve 2. Air. $\lambda_0 = 23.82$ cm. Curve 3. Water. *3a*, interference curve for crystal C_2, Fig. 1, *3b*, reaction on plate current of positive grid tube transmitter, *3c*, interference curve for crystal C_1, Fig. 1. From curves *3a*, *3b* and *3c*, mean $\lambda = 1.89$ cm.

[5] Miesowicz, Bull. Acad. Polonaise Sci. et Lettres **3–4A**, 95 (1934).
[6] Potapenko, Phys. Rev. **39**, 625; **40**, 988; **41**, 216 (1932).
[7] Kilgore, Proc. Inst. Rad. Eng. **20**, 1741 (1932).
[8] Megaw, Inst. Elect. Eng., London **72**, 313 (1933).
[9] Cleeton and Williams, Phys. Rev. **45**, 234 (1934).
[10] Wolff, Linder and Baden, Proc. Inst. Rad. Eng. **23**, 11 (1935).
[11] McPherson and Ullrich, Inst. Elect. Eng., London **78**, 629 (1936).

Results

Table I gives a summary of results for each wave-length and Fig. 3 shows the index of refraction for water, plotted against frequency. The two positive grid tubes had almost the same wave-length. They offered the added advantage of a third indication of interference, exhibited as reaction in the plate circuit of the oscillator itself as the water level was varied. This reaction is objectionable, however, and may introduce an error which could account for the fact that neither of the points determined with these tubes fall on the curve described by the magnetron points in Fig. 3.

The water temperature, recorded in Table I, was not the same for all the runs, but correction for this difference[12] would not shift the points appreciably in Fig. 3. The variation of index of refraction with temperature for long radio waves amounts to 0.23 percent decrease in index per degree increase in temperature. The extreme points on this curve were taken at the same temperature.

Conclusions

Fig. 3 shows a decrease of the index of refraction of water with increasing frequency, in agreement with the suggestions of Debye[3] and Bernal and Fowler.[4] However, the absolute value of the index at the low frequency end of the curve is greater than that given by $\mu=\sqrt{\epsilon}=\sqrt{81}$, where ϵ is the dielectric constant of water for frequencies of the order of a megacycle. An examination of curves 1 and 2 of Fig. 2 at once suggests that the air wave-lengths for the longer

Table I. *Summary for H_2O.*

Run No.	Mean λ_0(cm) in air	Mean λ(cm) in H_2O	Temp. °C	Tube used	$\mu=\frac{\lambda_0}{\lambda}$	$p=\frac{3\times10^{10}}{\lambda_0}$
I	23.82	2.45	28	Magnetron #1	9.73	12.6×10^8
II	17.76	1.88	23	Magnetron #1	9.44	16.9
III	17.42	1.89	23	Positive grid #1	9.23	17.2
IV	17.02	1.85	24	Positive grid #2	9.22	17.6
V	12.65	1.40	21	Magnetron #1	9.04	23.7
VI	11.48	1.30	25	Magnetron #2	8.83	26.2
VII	8.53	1.02	28	Magnetron #2	8.36	35.1

[12] Lattey, Gatty and Davies, Phil. Mag. **12**, 1019 (1931).

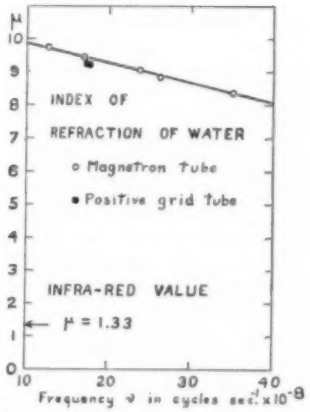

Fig. 3. Refractive index μ for H_2O.

waves are not so accurate as for the shorter waves, due to the experimentally limited motion of the wave meter, allowing only a few peaks to be obtained for large λ while many could be obtained for small λ. The type of anomalous dispersion discussed by Debye[3] for this spectral region would lead to a monotonically decreasing value of μ with increasing frequency as shown in the *International Critical Tables*.[13] However, the experimental curve of Fig. 3 indicates a rise in the refractive index in the region between low frequencies and those employed here, and thus indicates a departure from the theory.

It is anticipated that a colleague in this work will carry out plans to investigate this method further. A beat frequency method of wave-length comparison should prove valuable.

The method employed here should be applicable to the study of the index of refraction of many fluids having low conductivity.

Acknowledgment

I am grateful to the staff of the Biological Laboratory at Cold Spring Harbor for granting me facilities to complete this work there. I deeply appreciate the keen interest and suggestions given all during this research by Professor Collins and Dr. Bedell of the department of physics at Cornell University, where the work began.

[13] *International Critical Tables* **6**, 77 (1929).

Approximately Relativistic Equations for Nuclear Particles

G. BREIT
University of Wisconsin, Madison, Wisconsin
(Received November 9, 1936)

Cosmic-ray showers indicate that at high energies interaction between nuclear particles is concerned with the creation and destruction of matter. It may, therefore, be expected that a complete relativistic theory of nuclear forces will involve explicit reference to the phenomena described at present as the electron-neutrino field. Theories of this kind are still too incomplete and self-contradictory to be reliable in practical work. It is, nevertheless, possible to set up equations which are relativistically invariant for transformations involving low velocities. Such equations form the subject of the present report. They are restricted to energies of relative motion that are small in comparison with the rest mass. By means of them it should be possible to discuss relativistic effects for ordinary nuclear energy levels. Possible forms of classical equations contain an interaction energy between two particles in the form given by Eq. (13.2). Here a, b are arbitrary real constants. The vector from particle 1 to particle 2 is $\mathbf{r}$, the velocities of the particles are $\mathbf{v}_1$, $\mathbf{v}_2$, the velocity of light is c. If $a=b=1$, one obtains a generalization of Darwin's equation, which describes the motion of electrically charged particles. For $a=-1$, $b=1$ particle 1 acts on particle 2 approximately as though it produced a scalar potential field responsible for the acceleration of particle 2. The requirement of invariance for wave equations of particles with spin (Pauli types) makes it necessary to have spin-orbit coupling which should give rise to the fine structure of nuclear levels. For ordinary interactions the spin-orbit energy may have the form given by Eq. (15.4), where b is an arbitrary real constant, $\mathbf{p}$ is the momentum and $\boldsymbol{\sigma}$ is Pauli's spin matrix. For $b_{ij}=-1$ one obtains the type of coupling taking place between extranuclear electrons. If $b_{ij}=1$ each particle interacts only with its own orbit as though it were moving in a scalar field. It is the latter hypothesis that is simplest and corresponds to $a=-1$, $b=1$ of the classical equation. Extensions of the above classifications have been made to the Majorana [Eqs. (15.7), (15.8)] and the Heisenberg [Eq. (15.9)] exchange interactions. The simplest type in the Majorana case appears to be in satisfactory agreement with experiment for Li^7 and agrees in order of magnitude with other cases. Extensions to Dirac's types of equations have been made. They lead one to expect coupling between spins of nuclear particles in apparent qualitative but not quantitative agreement with experiment for the deuteron. This agreement is not sufficiently good to establish a form of interaction energy but indicates a possibility of doing so in the future.

IT has been noticed by Inglis[1] that the apparent inversion of doublets in nuclei can be explained as a result of taking into account the effect introduced by Thomas in the discussion of the fine structure in atomic spectra. A nuclear particle, such as a neutron, is subjected to forces the actual nature of which is not known. There is no reason to consider these forces as being representable by an electromagnetic field and it is more likely that they owe their origin to the electron-neutrino phenomena. The direct influence of the electric field on the spin which is important for the fine structure of atomic spectra is thus presumably absent in nuclei. Very schematically one may consider a single nuclear particle as moving in the combined field of the other particles. In this rough approximation one may attempt to regard a single nuclear particle as exposed to the field of a scalar potential due to the remainder of the nucleus. This potential will be provisionally supposed to be a function of space-time and to be independent of the time in the coordinate system in which the nucleus is at rest. For such a model it follows that the Thomas term is the only one that exists for a neutron and that for a proton it should be combined with the effect of the electric field of the nucleus that is expected from the Dirac equation for a particle in a central field.

A proof of this has been already given by Furry,[10] who saw the possibility of inserting the scalar as an addition to the mass term mc^2 in Dirac's equation. The same result can be obtained by considering the transformation properties of wave functions. The latter method is desirable in order to bring out the connection with the treatment of many particles as well as in order to establish the interactions independently of special Dirac equations. It will be given in Section 1.

The neutrons and protons in a nucleus have approximately equal masses. In this respect the nucleus differs qualitatively from an atom which

is composed of a heavy nucleus and several light electrons. Even in an atom the spin-orbit interactions are describable by a central field only somewhat accidentally. The correct description must be made by considering interactions between all pairs of particles.[2] Calculation shows[3] that the naive central field picture is approximately correct mainly because electrons in inner shells are so firmly bound that their action on a valence electron is comparable with that of a static distribution of charge. No such simplicity is apparent in a nucleus. It is therefore desirable to understand what kind of spin-orbit and orbit-orbit interactions may be postulated. In Dirac's theory spin effects may usually be considered as of the order v^2/c^2 in comparison with the kinetic energy, where v is the velocity of the particle and c is the velocity of light. It is, therefore, reasonable to require that the theory of nuclear particles be relativistically invariant to this order. It is presumably impossible to have a completely relativistically invariant theory for the interaction between several particles with a finite range of force and without explicit reference to a field. It is superfluous, therefore, and probably fruitless in the discussion of the present problem to require complete invariance. In Section 2 possible classical interactions between particles will be discussed and enumerated. It will be found that those among them that have special physical interest form a two-parameter set. Two types deserve special mention. One of them is the most immediate extension of Darwin's equation for two charged particles interacting according to the laws of classical electrodynamics. The other corresponds to each particle setting up a scalar field in a reference system in which it is at rest. It is this type that is related most closely to the interaction discussed in Section 1. In Section 3 possible types of wave equations will be discussed. It will be seen that: (a) The presence of spin-orbit interactions is a general consequence of the transformation properties of wave functions; (b) Their exact form is not uniquely determined by the transformation properties, but all possible forms of physical interest may be considered as linear combinations of electromagnetic interactions with pure Thomas terms; (c) A possible extension of the scalar one-particle picture gives only the Thomas terms. The effect of Majorana and Heisenberg exchange will be also considered in this section.

1. One Particle

It will be supposed that the particle in its free state is describable by Dirac's equation. The fact that the magnetic moment of nuclear particles is not that given by Dirac's equation in its original form does not contradict this supposition, because it is possible to introduce in Dirac's equation direct interactions between the magnetic field and the magnetic moment in the manner proposed by Pauli.[4] The transformation properties of Dirac's equation are the same whether a true magnetic moment of the Pauli type is introduced or not. It is on the other hand questionable whether Dirac's equation or any of its modifications gives an exact account of the properties of nuclear particles. In fact high energy collisions involving relative velocities of nuclear particles comparable with c indicate from experiment,[5] in the light of Heisenberg's theory[6] of showers, the importance of processes involving the creation and destruction of particles. For this reason it is preferable to base theories of nuclear spin-orbit interactions on corrections of the order v^2/c^2 rather than on an exact form of a single particle equation.

The original discussion of Thomas does not apply directly to particles whose spin is describable by means of a Pauli or a Dirac equation. For a Dirac particle the spin is a secondary characteristic. As has been pointed out by Schroedinger,[7] a Dirac particle is unable to move uniformly in a straight line when left to its own devices. This property of the particle gives rise to the spin. It is, therefore, necessary to consider the Thomas term directly from the point of view of the wave equation rather than in terms of a classical analogy.

According to Dirac[8] the Lorentz transformation

$$\begin{aligned} &x' = x \operatorname{ch}\theta - ct \operatorname{sh}\theta, \qquad ct' = ct \operatorname{ch}\theta - x \operatorname{sh}\theta, \\ &p_x' = p_x \operatorname{ch}\theta - p_0 \operatorname{sh}\theta, \quad p_0' = p_0 \operatorname{ch}\theta - p_x \operatorname{sh}\theta, \\ &\operatorname{ch}\theta = (1 - v^2/c^2)^{-\frac{1}{2}}, \quad \operatorname{sh}\theta = (v/c)(1 - v^2/c^2)^{-\frac{1}{2}}; \\ &p_0 = E/c \quad (\operatorname{ch}\theta \equiv \cosh\theta,\ \operatorname{sh}\theta \equiv \sinh\theta) \end{aligned} \tag{1}$$

induces the transformation

$$\psi' = e^{\alpha_1\theta/2}\psi, \quad \psi'^* = \psi^* e^{\alpha_1\theta/2} \tag{2}$$

on the wave function. This means that the transformed wave function ψ' satisfies the Dirac equation in the transformed system K' and that all physical quantities calculated by means of ψ' in K' are related by relativistic formulas to corresponding quantities calculated by means of ψ in the original system K.

The Dirac equations can be written as

$$\begin{aligned}(p_0+Mc)\Phi+(\boldsymbol{\sigma}\mathbf{p})\Psi=0,\\ (p_0-Mc)\Psi+(\boldsymbol{\sigma}\mathbf{p})\Phi=0,\end{aligned} \tag{3}$$

where the σ are Pauli spin matrices, Ψ is the two-component Pauli wave function, and Φ is also a two-component wave function. Both Φ and Ψ are column matrices. The Dirac function ψ is a column matrix having the two elements of Φ in first and second place and the two elements of Ψ in third and fourth place. From (3) one obtains in sufficient approximation

$$\Phi = -(\boldsymbol{\sigma}\mathbf{p})\Psi/2Mc. \tag{3'}$$

This approximation is valid for interactions of both the electromagnetic and the scalar types. The occurrence of terms in the vector potential in (3) leads only to negligible corrections in (3') because these terms can be taken to be of the order e^2v/c^2r, where r is the distance between nuclear particles and v is the velocity. This quantity is of the order of mv for $r\sim e^2/mc^2$, where m is the electronic mass, while the operations involved in $-i\hbar\partial/\partial x$ give rise to Mv, where M is the nuclear particle mass. Similarly the addition of a scalar interaction energy to Mc^2 or of an electrostatic potential to p_0 gives rise to insignificant corrections for forces having the approximate range e^2/mc^2.

Using (3') in (2)

$$\Psi' = \{\mathrm{ch}\,(\theta/2) - (2Mc)^{-1}(\mathbf{p}+i[\mathbf{p}\times\boldsymbol{\sigma}])_x\,\mathrm{sh}\,(\theta/2)\}\Psi. \tag{4}$$

Let now the wave equation be of the form

$$\left\{\frac{\hbar}{i}\frac{\partial}{\partial t}+Mc^2+\frac{p^2}{2M}-\frac{p^4}{8M^3c^2}-J+Q\right\}\Psi=0. \tag{5}$$

Substituting Ψ in terms of Ψ' and expressing all other quantities in K in terms of quantities in K', the wave equation should return to its original form. It will be supposed that J is a scalar. It will thus transform into itself. The quantity Q is introduced into Eq. (5) in order to correct the remaining terms for lack of invariance. Instead of considering all of Eq. (4), it will be first approximated by

$$\Psi = S\Psi'; \quad S=1+i\mathbf{v}[\mathbf{p}\times\boldsymbol{\sigma}]/4Mc^2. \tag{4'}$$

This approximation neglects some effects of order v^2/c^2. However, an inspection of Eq. (4) shows that effects of order v^2/c^2 are additive and no essential error is committed.[9] Substituting Eq. (4') into Eq. (5) and multiplying by S^{-1} from the left one obtains on account of the presence of J the term

$$J-S^{-1}JS=(h/4Mc^2)[\boldsymbol{\nabla}J\times\boldsymbol{\sigma}]\mathbf{v}. \tag{6}$$

This term must be canceled by the introduction of a suitable term into Q. It will be supposed that Q contains only terms of order v^2/c^2. Therefore one may take $S^{-1}QS=Q$. Thus in the approximation of Eq. (4') there is a part Q_0 of Q such that $Q_0'-Q_0$ must be equal to the right side of Eq. (6). This can be accomplished by

$$Q_0 = -(h/4M^2c^2)[\boldsymbol{\nabla}J\times\boldsymbol{\sigma}]\mathbf{p}. \tag{6'}$$

This is the Thomas term which must, therefore, be included in order to enforce invariance. In addition it is possible to postulate the presence of other terms in σ entering Q. Such terms must form an invariant to the order v^2/c^2. It is impossible to form such an invariant by having ∇J, σ, and $\mathbf{p}$ entering the expression once. There exists, in consequence, no term which can be added to Q which has an essential relation to Q_0.

Transforming Eq. (5) to variables in K' one finds that

$$\left\{-E'+Mc^2+\frac{p'^2}{2M}-\frac{p'^4}{8M^3c^2}-J - \frac{v}{4Mc^2}(3p_z'J+Jp_z')-\frac{v^2}{2c^2}J + \frac{hv}{4Mc^2}[\boldsymbol{\nabla}'J\times\boldsymbol{\sigma}]_z+Q\right\}\Psi'=0. \tag{7}$$

The terms containing v have to be compensated by $Q-Q'$. A possible Q, determined in a manner analogous to that in Eq. (6′), gives an invariant form by substitution into Eq. (5)

$$\left\{-E+Mc^2+\frac{p^2}{2M}-\frac{p^4}{8M^3c^2}-J+\frac{p^2J+\mathbf{p}J\mathbf{p}}{4M^2c^2}\right.$$
$$\left.-\frac{h}{8M^2c^2}([\mathbf{p}\times\boldsymbol{\nabla}J]-[\boldsymbol{\nabla}J\times\mathbf{p}])\boldsymbol{\sigma}\right\}\Psi=0. \quad (8)$$

The term in $\boldsymbol{\sigma}$ is here symmetrized so as to be Hermitean. The terms in p^2J and $\mathbf{p}J\mathbf{p}$ form a non-Hermitean operator. This is due to the fact that the total probability of finding the particle is not given by the volume integral of $|\Psi|^2$ but by

$$\int\psi_\mu^*\psi_\mu d\tau=\int\Psi_\alpha^*(1+p^2/4M^2c^2)\Psi_\alpha d\tau \quad (8')$$
$$(\mu=1,\ 2,\ 3,\ 4;\ \alpha=1,\ 2).$$

It is possible, however, to transform the wave function Ψ so as to have a Hermitean operator. Thus if

$$\Psi^{(1)}=(1+p^2/8M^2c^2)\Psi \quad (9)$$

Eq. (8) becomes

$$\left\{-E+Mc^2+\frac{p^2}{2M}-\frac{p^4}{8M^3c^2}-J+\frac{p^2J+2\mathbf{p}J\mathbf{p}+Jp^2}{8M^2c^2}\right.$$
$$\left.-\frac{h}{8M^2c^2}([\mathbf{p}\times\boldsymbol{\nabla}J]-[\boldsymbol{\nabla}J\times\mathbf{p}])\boldsymbol{\sigma}\right\}\Psi^{(1)}=0, \quad (9')$$

which is Hermitean. The modified function $\Psi^{(1)}$ satisfies the simple normalization condition

$$\int\Psi_\alpha{}^{(1)*}\Psi_\alpha{}^{(1)}d\tau=\int\psi_\mu^*\psi_\mu d\tau=1, \quad (9'')$$

which follows from Eqs. (8′) and (9). An elegant treatment of the single particle problem due to Furry[10] can be carried out introducing the scalar $-J$ into the Dirac equation as an addition to the rest mass energy Mc^2. The equation in the Dirac form is

$$\{p_0+(\boldsymbol{\alpha}\mathbf{p})+\beta(Mc-J/c)\}\psi=0. \quad (10)$$

Expressing the components Φ in terms of Ψ by means of Eq. (3′) and substituting into the second Eq. (3) modified by $Mc\rightarrow Mc-J/c$, it is found that Ψ satisfies Eq. (8). This is a natural result inasmuch as Furry's Eq. (10) is strictly invariant. It should be noted that the transition from Eq. (7) to Eq. (8) is not unique. Thus it is possible to use instead of $p^2J+\mathbf{p}J\mathbf{p}$ in this equation the quantity $(3p^2J+Jp^2)/2$ without changing the transformation properties, and more generally an arbitrary constant times $p^2J+Jp^2-2\mathbf{p}J\mathbf{p}$ can be added to $p^2J+\mathbf{p}J\mathbf{p}$. There is thus a greater freedom in the forms of two-component equations invariant to order v^2/c^2 than is apparent from Eq. (10). The equations obtained in this manner are identical, however, from the point of view of classical analogy, and in the absence of another clue it is impossible to give reasons for preferring one to another. The particular form (8) may perhaps be advocated on the grounds that it is equivalent to Eq. (10).

It is possible to add to the operators in Eqs. (8), (9′) any quantity invariant to order v^2/c^2. Thus J^2/Mc^2 multiplied by a reasonably small number may be added. The addition of a term in this quantity is, however, only of trivial interest in the present case because such a term may be considered as being incorporated in J. The addition of commutator-like terms such as $(p^2J+Jp^2-2\mathbf{p}J\mathbf{p})/Mc^2$ amounts to adding terms in derivatives of J and also offers no essentially new possibility. Terms in p^2J and $\mathbf{p}J\mathbf{p}$ can occur only as in Eq. (8) to within the freedom of adding a commutator. Using p^2 and p^4 it is impossible to have an invariant except that already occurring in the equation. Within the above discussed set of the simplest possibilities, Eqs. (8) and (9′) are thus essentially unique.

The parts of the operators occurring in Eqs. (8), (9′) which do not contain $\boldsymbol{\sigma}$ can be interpreted as corresponding to the wave equation of a particle without spin, invariant to order v^2/c^2. The verification is analogous to the step from Eq. (7) to Eq. (8). A slight difference from Eq. (8) is found in the order of factors. Allowing the wave function to transform itself by

$$\Psi^{0\prime}=(1+v^2/4c^2-vp_x/2Mc^2)\Psi^0 \quad (11)$$

it is found that

$$\left\{-E+Mc^2+\frac{p^2}{2M}-\frac{p^4}{8M^3c^2}-J+\frac{\mathbf{p}J\mathbf{p}}{2M^2c^2}\right\}\Psi^0=0 \quad (11')$$

is an invariant form.

The transformation of Eq. (11) gives

$$[\Psi^{0*}\Psi^0]' = \left(1+\frac{v^2}{2c^2}\right)\Psi^{0*}\Psi^0 - \frac{hv}{2iMc^2}\left(\Psi^{0*}\frac{\partial\Psi^0}{\partial x}-\Psi^0\frac{\partial\Psi^{0*}}{\partial x}\right).$$

One may, therefore, interpret $\Psi^{0*}\Psi^0$ as the particle density and use the normalizing condition

$$\int \Psi^{0*}\Psi^0 d\tau = 1. \qquad (11'')$$

In obtaining Eq. (8) it was supposed that the contributions due to time derivatives of J arising in the transformations are small. This requirement can be satisfied by supposing that there exists a frame of reference in which J is a function only of space and does not depend on time. This frame may be called the rest frame. The other frames considered above are those obtained by the application of a small translational velocity to the rest frame. For such transformations ∇J is an invariant since it changes only by terms of order $(v^2/c^2)\nabla J$ on transformation. If J is only a function of the distance r from a fixed point there is no necessity of symmetrizing the last term containing σ because then

$$[\mathbf{p}\times\nabla J] = -[\nabla J\times\mathbf{p}].$$

If J, instead of transforming as a scalar, transforms as the time component of a four-vector, one obtains essentially the same results as are derivable from the ordinary Dirac equation.

2. Classical Equations for Several Particles

It will be supposed that the system can be treated by means of a variational equation,

$$\delta\int L dt = 0. \qquad (12)$$

The trajectory of the dynamical system in the reference system K corresponds to segments of world lines in an interval $t_1<t<t_2$. The Lagrangian L will be supposed to be given approximately by

$$L_0 = \sum_i M_i v_i^2/2 + \sum_{i>j} J_{ij}(r_{ij}), \qquad (12')$$

where M_i are the masses, v_i the velocities of the particles, and r_{ij} are the distances between them. In addition to L_0 the function L will be supposed to contain terms of the order $(v^2/c^2)L_0$. These terms will now be determined by the requirement that Eq. (12) should determine the same world lines independently of the coordinate system used. For a system of noninteracting particles ($J_{ij}=0$) there is an obvious solution corresponding to describing each particle separately. In this case one may use

$$L_0 = \sum_i M_i c^2[1-(1-v_i^2/c)^{21}].$$

Expanding each term of this sum one obtains

$$L_0 = \sum_i M_i(v_i^2/2+v_i^4/8c^2) \quad (J=0)$$

to the required order. For this L_0 the integral in Eq. (12) is not invariant because: (a) each term of the sum contains $M_i c^2\int dt$ which is not invariant. However, the variation of this quantity is zero and its inclusion is harmless. (b) In the transformation $K\rightarrow K'$ it is impossible to deal with identical segments of world lines in both systems. If the end points of the world line for i are kept the same, those of j have to be changed in K' from what they were in K. This circumstance also does not matter because the variations of the coordinates of i and j are supposed to be independent of each other. Therefore the variations over that portion of the world line of j which is common to K and K' for fixed end points of the world line of i are automatically the same as long as each term of Ldt is invariant. It is thus seen that the invariance of Ldt is sufficient for the invariance of the world lines. It is obviously not a necessary condition as is seen in the case of the addition of terms in $\int dt$.

The terms J_{ij} substituted into Eq. (12) give rise to noninvariant quantities. These will now be calculated. It will be supposed that in calculating the correction terms it is legitimate to neglect the curvature of the world lines. This assumption does not follow from considerations of invariance. It simplifies the discussion by preventing the explicit occurrence of accelerations in the Lagrangian. For electromagnetic

interactions it leads to neglecting radiation reactions. For nuclear forces it amounts to neglecting $x\ddot{x}/c^2 \sim J/Mc^2 \sim 20m/M \sim 10^{-2}$ in comparison with unity. Here m is the electronic mass. In terms of this estimate the approximation is a good one since the effects neglected are of the order of 10^{-2} times the correction terms in v^2/c^2.

For the transformation given by Eq. (1) the distances between particles 1,2 in K' and K are related by

$$r' = r - \frac{(\mathbf{vr})^2}{2c^2 r} + \frac{(\mathbf{vr})}{c^2 r}\,\frac{M_1(\mathbf{rv}_2)+M_2(\mathbf{rv}_1)}{M_1+M_2}$$

and hence

$$J(r') = J(r) + \left[-\frac{(\mathbf{vr})^2}{2c^2} + \frac{(\mathbf{vr})}{c^2}\,\frac{M_1(\mathbf{rv}_2)+M_2(\mathbf{rv}_1)}{M_1+M_2}\right]\frac{dJ}{rdr}. \tag{13}$$

In order that Ldt be invariant it is necessary that L should transform as ds/dt where ds is the differential of the four dimensional distance. The transformation formulas for ds/dt are different for the world lines of 1 and 2. The world line of the center of gravity of 1 and 2 gives a still different transformation of ds/dt. At this stage, therefore, the definition of the world line is still arbitrary, since one has the above three choices, each of which has some physical plausibility. This arbitrariness of the choice of the world line would destroy the possibility of having a sensible description of the system by means of Eq. (12) if it were not for the fact that the results of Eq. (12) are independent of the choice in the following sense. Let M_1, M_2 in Eq. (13) be given arbitrary values and let the same values be used for the definition of the path of the center of gravity. Let the transformation of L be similar to that of ds/dt along this path of the center of gravity. The results of Eq. (12) will be seen to be independent of the values of M_1 and M_2. This means that it is possible to use either the path of 1 or that of 2 and that the results of the two procedures are consistent.

For the path of the center of gravity for the transformation of Eq. (1)

$$\frac{ds}{dt'} = \left[1 - \frac{v^2}{2c^2} + \frac{M_1(\mathbf{vv}_1)+M_2(\mathbf{vv}_2)}{(M_1+M_2)c^2}\right]\frac{ds}{dt}. \tag{13'}$$

It is now required that $J-Q$ should transform as ds/dt. Since Q contains by definition only terms of order v^2/c^2, the transformation formula for Q is determined by means of Eqs. (13), (13'). It is

$$Q - Q' = \left[-\frac{v^2}{2c^2} + \frac{(\mathbf{vv}_1)+(\mathbf{vv}_2)}{2c^2}\right]J + \left[\frac{(\mathbf{vr})^2}{2c^2} - \frac{(\mathbf{vr})}{2c^2}((\mathbf{v}_1+\mathbf{v}_2)\cdot\mathbf{r})\right]\frac{dJ}{rdr} + \frac{M_1-M_2}{2c^2(M_1+M_2)}\,\frac{d}{dt}[(\mathbf{rv})J], \text{ where } \mathbf{r}=\mathbf{r}_1-\mathbf{r}_2. \tag{13''}$$

The last term in Eq. (13'') may be disregarded because in Eq. (12) it gives rise only to a function of the end points of the path. The remainder of $Q-Q'$ is independent of M_1 and M_2 and is equal to $Q-Q'$ for $M_1=M_2$. It is symmetric in the coordinates and velocities of 1 and 2. It is natural to look for possible Q which are also symmetric in 1 and 2. Unsymmetric Q are either reducible to symmetric Q by the addition of a complete differential to Ldt or else they imply a different action of particle 1 on particle 2 from that of 2 on 1. Such a law of interaction is improbable and will not be considered here. Only symmetric possibilities for Q will be discussed.

A possible $J-Q$ with Q transforming itself as in Eq. (13'') is

$$J - Q = J - [(\mathbf{v}_1\mathbf{v}_2)J - (\mathbf{v}_1\mathbf{r})(\mathbf{v}_2\mathbf{r})dJ/rdr]/4c^2, \tag{13.1}$$

as is verified by applying the transformation of Eq. (1) and observing that for the transformation of Q it is sufficient to use Newtonian rather than relativistic addition of velocities and to consider r as invariant in this connection. All other Q can be obtained from Eq. (13.1) by the addition of invariants. In this way one obtains among other possibilities the following expression for $J-Q$:

$$J - Q = J - \{2a(\mathbf{v}_1\mathbf{v}_2) + (1-a)(v_1^2+v_2^2)\}J/4c^2 + \{2b(\mathbf{v}_1\mathbf{r})(\mathbf{v}_2\mathbf{r}) + (1-b)[(\mathbf{v}_1\mathbf{r})^2 + (\mathbf{v}_2\mathbf{r})^2]\}dJ/4c^2 rdr, \tag{13.2}$$

where a and b are arbitrary real constants. For $a=b=1$, Eq. (13.2) agrees with Eq. (13.1). In this case the Lagrangian L_0+J-Q is a generalization of that obtained by Darwin for electromagnetic interactions, as is seen by substituting e^2/r for J. It will be recalled that Darwin's approach was that of retarded potentials and that the Lagrangian was found by: (a) working out the equations of motion for particle 1 using position and velocity of 2 as parameters, (b) finding the Lagrangian for 1, and (c) showing that there exists another symmetrical Lagrangian differing from the first one by a time derivative. It is desirable to explain why Darwin's equation is of type (13.1) rather than of some other type contained in Eq. (13.2). Obviously the distinguishing feature of the form (13.1) is that of antisymmetry with respect to reversal of sign of one of the velocities. All other types in Eq. (13.2) have another type of symmetry. In the electromagnetic case corrections for the velocity $\mathbf{v}_1$ enter for two reasons. In the first place particles 1 and 2 interact magnetically. This interaction is antisymmetric in $\mathbf{v}_1$ because it depends on $(\mathbf{v}_1\mathbf{v}_2)$. In the second place corrections for retardation must be made. These corrections can depend on the direction of motion of 1, while one discusses the motion of 2 only because 1 is moving away or towards 2. Hence again the addition to the Lagrangian must be antisymmetric in $\mathbf{v}_1$.

It can be verified by explicit calculation that the forms given by Eq. (13.2) give an expression for the force which is in agreement with relativity kinematics to the order v^2/c^2. According to relativity if $\mathbf{P}_1$ stands for $M_1\mathbf{v}_1(1-v_1^2/c^2)^{-1/2}$ then at the same point in space time the rates of change of $\mathbf{P}_1$ and $\mathbf{P}_1'$ in K and K' are connected by

$$\dot{\mathbf{P}}_1=\dot{\mathbf{P}}_1'+[-v^2\dot{\mathbf{P}}_1'+\mathbf{v}(\mathbf{v}\dot{\mathbf{P}}_1')]/2c^2 \qquad (14)$$
$$\left(\frac{dx'}{dt'}=\frac{dy'}{dt'}=\frac{dz'}{dt'}=0\right),$$

where $\mathbf{v}$ is the transformation velocity, provided terms of order higher than v^2/c^2 are neglected and provided $\mathbf{P}_1'=0$. The forces on 1 are thus determinable in terms of the force in that frame in which 1 is instantaneously at rest. The verification of Eq. (14) is straightforward but somewhat lengthy and is not reproduced here. It involves no approximations except that of neglecting all terms of order higher than v^2/c^2.

If one sets $a=b=0$ in Eq. (13.2) a simple form for $J-Q$ is obtained:

$$J-Q=J-\frac{v_1^2+v_2^2}{4c^2}J+\frac{1}{4c^2}[(\mathbf{v}_1\mathbf{r})^2+(\mathbf{v}_2\mathbf{r})^2]\frac{dJ}{rdr}. \qquad (14.1)$$

This is somewhat related to Eqs. (9′), (11′) for a single particle but does not quite correspond to them. Thus if particle 2 has a sufficiently large mass to make v_2 small at all times, the above $J-Q$ is not altogether equivalent to $J-v^2J/2c^2$ because

$$v_1^2J+(\mathbf{v}_1\mathbf{r})^2dJ/rdr=(d/dt)[(\mathbf{v}_1\mathbf{r})J]-(\dot{\mathbf{v}}_1\mathbf{r})J$$

and is not a complete differential. Working out the equations of motion for Eq. (14.1) and comparing them with the equations of motion following from Eqs. (9′), (11), no simple correspondence is found.

A simple correspondence is found, however, setting $a=-1$, $b=1$. In this case

$$J-Q=J-(\mathbf{v}_1-\mathbf{v}_2)^2J/2c^2-(\mathbf{v}_1\mathbf{v}_2)J/2c^2$$
$$+(\mathbf{v}_1\mathbf{r})(\mathbf{v}_2\mathbf{r})dJ/2c^2rdr \qquad (14.2)$$
$$(a=-1,\ b=1).$$

If $\mathbf{v}_2=0$, this agrees with Eqs (9′), (11′). Comparing the equations of motion following from Eq. (14.2) with those from Eq. (9′), it is found in both cases that in the reference system in which 2 is at rest the acceleration of 1 is the same function of its position with respect to 2 and its velocity. One may, therefore, regard Eq. (14.2) as being a generalization of Eq. (9′) and of Eq. (10) if in the latter the effect of the spin is neglected. One may think of Eq. (14.2) as giving such a motion of the two particles as corresponds to particle 2 producing in its reference system a scalar field which acts on particle 1, and the other way around.

Only two particles are explicitly considered above. The arguments which lead to Eq. (13″) for $Q-Q'$ can be generalized to any number of particles having arbitrary interactions in pairs. The calculation is more lengthy but the result is simply that, to within a term which is a complete

time derivative, $Q-Q'$ is a sum over pairs of terms such as are given by Eq. (13″) for a single pair. An extension of Eq. (14.2) to many particles is obtained by using a sum over pairs of such expressions. If particles 2, 3, $\cdots$ n are tied by strong forces into a large mass approximately at rest and particle 1 moves in their field, this generalization becomes equivalent to Eq. (9′) because the time average of $\mathbf{v}_2, \mathbf{v}_3, \cdots \mathbf{v}_n$ can be considered to be 0.

The forms used in Eq. (13.2) can be generalized by the addition of other invariants. Thus one could add terms in $(\mathbf{v}_1-\mathbf{v}_2)^2 r dJ/c^2 dr$ or in $((\mathbf{v}_1-\mathbf{v}_2)\mathbf{r})^2 J/c^2 r^2$. The use of such terms cannot be eliminated by general principles but appears to be an unnecessary complication. Similarly one can add terms in higher derivatives of J, and it is possible to have approximate invariants of order of magnitude v/c which in Lorentz transformation undergo changes only of order v^3/c^3.

3. Wave Equations for Many Particles

General methods for setting up relativistic equations for composite systems have been given by Heisenberg and Pauli, Fermi, Dirac, and Dirac, Fock and Podolsky.[11] These methods do not apply directly to the problem considered here because they are concerned with exact rather than approximate invariance. The approach of Heisenberg and Pauli by means of an invariant Lagrange function can nevertheless be made use of in a modified form. Instead of extending the integration over space time as is done by them it is more natural to consider here variational integrals over the time and the configuration space because this is the simplest formulation of a nonrelativistic equation. Speaking of the motion classically, it may be expected that the interaction energy J should be treated as small. Otherwise the velocity of at least one particle will be large and an approximate relativistic treatment will have no sense. This assumption corresponds to the similar restriction of small accelerations made in the classical case when Hamilton's principle was used. Forms of

$$\delta \int \mathfrak{L} d\tau = 0, \quad d\tau = dV_1 dV_2 \cdots dV_n dt \qquad (15)$$

will be looked for. Here $dV_1, dV_2, \cdots dV_n$ are elements of volume for each particle. If the interactions are not of an exchange type and if the particles have no spin, it may be expected that the resultant wave equations should have a possible classical form such as one of the forms in Section 2. Only the occurrence of commutators in the wave equations will, therefore, become clearer in such a discussion. The presence of terms in the spin-orbit and spin-spin interactions and of the effect of exchange is, on the other hand, obtainable from Eq. (15) and cannot be inferred from a classical discussion.

It will be supposed that if $c \to \infty$ in $\mathfrak{L}$ and the corresponding wave equation, the system will be invariant under Galilean transformations. Thus for exchange interactions it will be simplest to confine oneself to particles of equal masses. In discussing Lorentz invariance it is easiest to consider

$$\mathfrak{L} = \sum_i \mathfrak{L}_i + \sum_{i>j} \mathfrak{L}_{ij} \qquad (15.1)$$

and to require that (a) the forms $\mathfrak{L}_i$ should yield invariant equations for the separate particles and (b) all the $\int \mathfrak{L}_{ij} d\tau$ should be invariant when one substitutes into $\mathfrak{L}_{ij}$ arbitrary linear combinations of products of single particle wave functions, each single particle wave function being assumed here to obey the wave equation of a free particle. Assuming Eq. (15.1), the restriction (b) will formally give a correct treatment only for very small J. Nevertheless, it may be expected to be also applicable, to some extent, also in cases of reasonably large J, because the largest part of the interaction energy will be Galileo invariant. Regarding the interaction energy as a power series in $1/c$, the first term of it will be thus correct by assumption and the remaining term will be established only for small J. This is less than one might wish to attain but it is not much worse than the knowledge of corresponding terms for interactions between charged particles. The discussion of the classical spinless equations by means of their equations of motion showed that even though the assumption of small accelerations was made in using the variational principle, the transformation formulas for the force are formally invariant to the order v^2/c^2 independently of this assumption. Since the classical equations are better than expected it is possible that the wave equations behave similarly.

As in Eq. (4′) one may discuss the spin-orbit interactions separately. Corresponding to Eq. (3) one now has 2^n equations, where n is the number of particles. Instead of Eq. (2), one has for non-interacting particles a transformation in which the exponential function of Eq. (2) is replaced by a product of similar exponentials. Eq. (3′) is replaced by n equations which determine those wave function components in which the Dirac indices for just one particle are in the small group, (1, 2). The extension of Eq. (2) gives similar extensions of Eqs. (4), (4′) in which there occur sums over $[\mathbf{p}_i\times\boldsymbol{\sigma}_i]$. In this way instead of Eq. (6) one has

$$Q_0'-Q_0=\sum_{i,\,j}(h/4M_ic^2)[\boldsymbol{\nabla}_iJ_{ij}\times\boldsymbol{\sigma}_i]\mathbf{v}. \quad (15.2)$$

This equation is satisfied by

$$Q_0=-\sum_{i,\,j}(h/4M_ic^2)[\boldsymbol{\nabla}_iJ_{ij}\times\boldsymbol{\sigma}_i]\cdot\sum_k a_{ik}\mathbf{p}_k/M_k;\qquad \sum_k a_{ik}=1 \quad (15.3)$$

and the a_{ik} are so far arbitrary. Since it was decided to use for $J-Q$ only interactions of particles in pairs, since the occurrence of $\mathbf{p}_k/M_i$ in the interaction energy is strange, and since finally it is simplest to suppose that the interaction energy of a pair is symmetric, the following form is sufficiently general for most purposes:

$$\begin{aligned}Q_0=-\sum_{i>j}(h/4c^2)\{&[\boldsymbol{\nabla}_iJ_{ij}\times\boldsymbol{\sigma}_i][b_{ij}\mathbf{p}_i/M_i^2\\&+(1-b_{ij})\mathbf{p}_i/M_iM_j]+[\boldsymbol{\nabla}_jJ_{ij}\times\boldsymbol{\sigma}_j]\\&\cdot[b_{ij}\mathbf{p}_i/M_j^2+(1-b_{ij})\mathbf{p}_i/M_iM_j]\}. \quad (15.4)\end{aligned}$$

The b_{ij} may be different for every pair. For electromagnetic interactions[2] $b_{ij}=-1$, so that $2\mathbf{p}_2-\mathbf{p}_1$ goes with $\boldsymbol{\sigma}_1$. For $b_{ij}=1$ an extension of Eq. (9′) is obtained, as is readily verified by letting all M_j but one become infinite. Since J_{ij} is a function only of r_{ij}, Eq. (15.4) gives a Hermitean operator for Q_0.

If the interaction is of the Majorana type, it is simplest to take the masses as equal to each other because otherwise the operator must be modified in order to preserve Galilean invariance. One obtains

$$Q_0'-Q_0=(\mathbf{v}/8Mc^2)\sum_{k>l}[\mathbf{A}_{kl}\times(\boldsymbol{\sigma}_k-\boldsymbol{\sigma}_l)] \quad (15.5)$$

with

$$\mathbf{A}_{kl}=i[(\mathbf{p}_k-\mathbf{p}_l)J_{kl}+J_{kl}(\mathbf{p}_k-\mathbf{p}_l)]P_{kl}^M, \quad (15.6)$$

where P_{kl}^M is the Majorana operator exchanging the space coordinates of k and l. Possible forms for Q_0 are given by

$$\begin{aligned}Q_0&=\sum_{k>l}\left(\frac{-1}{8M^2c^2}\right)[a\mathbf{p}_k+(1-a)\mathbf{p}_l][\mathbf{A}_{kl}\times\boldsymbol{\sigma}_k]\\&=\sum_{k>l}\left\{\frac{ia}{4M^2c^2}[\mathbf{p}_k\times J_{kl}P_{kl}^M\mathbf{p}_k]\boldsymbol{\sigma}_k\right.\\&\qquad\left.-\frac{i(1-a)}{4M^2c^2}[\mathbf{p}_k\times J_{kl}P_{kl}^M\mathbf{p}_k]\boldsymbol{\sigma}_l\right\}, \quad (15.7)\end{aligned}$$

where a is a real constant. In this case J_{kl} rather than just dJ_{kl}/dr_{kl} enters into Q_0. Thus for $a=1$ and $a=0$, respectively,

$$\begin{aligned}(a=1)\quad Q_0&=\sum_{k>l}\left\{\frac{h}{4M^2c^2}(\boldsymbol{\nabla}_kJ_{kl})[\mathbf{p}_l\times\boldsymbol{\sigma}_k]\right.\\&\qquad\left.+\frac{i}{4M^2c^2}J_{kl}[\mathbf{p}_k\times\mathbf{p}_l]\boldsymbol{\sigma}_k\right\}P_{kl}^M,\\(a=0)\quad Q_0&=\sum_{k>l}\left\{\frac{h}{4M^2c^2}(\boldsymbol{\nabla}_kJ_{kl})[\mathbf{p}_k\times\boldsymbol{\sigma}_k]\right.\\&\qquad\left.+\frac{i}{4M^2c^2}J_{kl}[\mathbf{p}_k\times\mathbf{p}_l]\boldsymbol{\sigma}_k\right\}P_{kl}^M.\end{aligned} \quad (15.8)$$

For $a=1$ the value of Q_0 may be thought of as

$$\begin{aligned}(a=1)\quad Q_0&=-\frac{h}{4M^2c^2}\sum_i[\mathbf{p}_i\times\dot{\mathbf{p}}_i]\boldsymbol{\sigma}_i\\&=\frac{h}{4M^2c^2}\sum_i[\dot{\mathbf{p}}_i\times\mathbf{p}_i]\boldsymbol{\sigma}_i \quad (15.8')\end{aligned}$$

and corresponds therefore most closely to the expectation on classical theory. From the point of view of Eq. (15.8′) the choice $a=1$ is the simplest. It should be noted that with Majorana interactions $\dot{\mathbf{p}}_i/M$ is only approximately the acceleration. If classical analogy were followed literally, Eq. (15.8′) would be more complicated because the operator representing the acceleration contains many terms. The expression for it can be substituted for $\dot{\mathbf{p}}_i/M$ in Eq. (15.8′). However, there appears to be little justification for such a literal use of the Thomas term, particularly

since $\mathbf{p}_i/M$ does not represent the velocity. For exchange interactions involving Heisenberg's operator,

$$Q_0=-\frac{\hbar}{4M^2c^2}\sum_{k\gtrless l}[a\mathbf{p}_k+(1-a)\mathbf{p}_l]\cdot[\nabla_k J_{kl}\times\boldsymbol{\sigma}_k]P_{kl}{}^H. \quad (15.9)$$

Possible forms for Q can be discussed analogously to the classical Eqs. (13.2) introducing the momenta and spins into the equations. The discussion is somewhat simpler, however, if instead one uses equations of Dirac's type with the Hamiltonian given by

$$H=-c(\boldsymbol{\alpha}_1\mathbf{p}_1)-c(\boldsymbol{\alpha}_2\mathbf{p}_2)-(\beta_1+\beta_2)Mc^2-J+Q \quad (16.1)$$

as well as

$$H=-c(\boldsymbol{\alpha}_1\mathbf{p}_1)-c(\boldsymbol{\alpha}_2\mathbf{p}_2)-(\beta_1+\beta_2)Mc^2-\beta_1\beta_2J+Q \quad (16.2)$$

in the customary notation.

It is also possible to combine the two types and to have J occur partly with $\beta_1\beta_2$ and partly by itself. It will first be shown that Eq. (16.1) is satisfactory with

$$Q=\tfrac{1}{2}(\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2)J-\tfrac{1}{2}(\boldsymbol{\alpha}_1\mathbf{r})(\boldsymbol{\alpha}_2\mathbf{r})(dJ/rdr). \quad (16.3)$$

Only the contributions due to $J-Q$ to the integral in Eq. (15) need be considered since the other terms give an invariant contribution. The Lorentz frame K is changed to K'. The integral in K' will be evaluated by comparison with the integral in K. The world point (1) corresponding to (t, x_1, y_1, z_1) will be kept fixed temporarily. In K, dV_2 at a world point A corresponds then to the same time t. In K', however, the point $(t, x_1, y_1, z_1)=(t', x_1', y_1', z_1')$ occurs in the integral together with points $B=(t', x_2', y_2', z_2')$ which, therefore, have values of t different from that of (1). Let the points B be associated to the points A by having $(x, y, z)_B=(x, y, z)_A$. Then

$$dx_B'=(1-v^2/c^2)^{\frac{1}{2}}dx_A,\quad y_B'=y_B,\quad z_B'=z_B;$$
$$t_B-t_A=(v/c^2)(x_2-x_1);$$
$$J(\mathbf{r}_B'-\mathbf{r}_1')=J(r)-\frac{v^2}{2c^2}\frac{(x_2-x_1)^2}{r}\frac{dJ}{dr}, \quad (16.4)$$

where quantities without suffixes refer to system K. Consider a wave function $\psi_{\mu\nu}=\varphi_\mu\chi_\nu$, where φ depends only on 1 and χ depends only on 2. Then, using the conservation theorem for particle density, it is found, on neglecting all terms of order higher than v^2/c^2, that

$$(\chi'^*\chi')_B=\left[\left(1+\frac{v^2}{2c^2}\right)(\chi^*\chi)+\frac{v}{c}(\chi^*\alpha^1\chi)+\frac{v}{c}(x_2-x_1)\frac{\partial(\chi^*\alpha^k\chi)}{\partial x_2{}^k}\right]_A, \quad (16.5)$$

where $(\alpha^x, \alpha^y, \alpha^z)=(\alpha^1, \alpha^2, \alpha^3)$ and $(x, y, z)=(x^1, x^2, x^3)$. The symbol $(\chi^*Y\chi)$ stands for $\chi_\mu{}^*Y_{\mu\nu}\chi_\nu$. From now on the suffix A is omitted where no confusion is caused. From Eqs. (16.4) and (16.5) it follows that

$$\int(\chi_B'^*J(\mathbf{r}_B'-\mathbf{r}_1')\chi_B')dV_B'=\int\left(\chi^*\left[J-\frac{vx}{c}\frac{(\mathbf{r}\boldsymbol{\alpha}_2)}{r}\frac{dJ}{dr}-\frac{v^2}{2c^2}\frac{x^2}{r}\frac{dJ}{dr}\right]\chi\right)dV_2$$

and

$$\left[\int(\psi^*J\psi)dV_2\right]_B'=\int\left(\psi^*\left[J-\frac{vx}{c}\frac{(\mathbf{r}\boldsymbol{\alpha}_2)}{r}\frac{dJ}{dr}-\frac{v^2}{2c^2}\frac{x^2}{r}\frac{dJ}{dr}+\frac{v^2}{2c^2}J+\frac{v}{c}\alpha_1{}^xJ\right]\psi\right)dV_2,$$

where $\mathbf{r}=(x, y, z)=(x_2-x_1, y_2-y_1, z_2-z_1)$. (16.6)

Using Q of Eq. (13.3)

$$\left[\int(\psi^*Q\psi)dV_2\right]'=\int(\psi^*Q\psi)dV_2+\int\left(\psi^*\left[\frac{v}{2c}(\alpha_1{}^x+\alpha_2{}^x)J+\frac{v^2}{2c^2}J-\frac{vx}{2c}((\boldsymbol{\alpha}_1+\boldsymbol{\alpha}_2)\mathbf{r})\frac{dJ}{rdr}-\frac{v^2x^2}{2c^2}\frac{dJ}{rdr}\right]\psi\right)dV_2.$$

On the left side the $'$ means that *all* quantities are evaluated in K'. Combining this with Eq. (16.6) and using the transformation formula for $\varphi^*\varphi$ it is found that

$$\left[\int(\psi^*[J-Q]\psi)dV_2\right]'=\int\left(\psi^*\left\{J-Q+\frac{v}{2c}\frac{\partial}{\partial x}[\mathbf{r}(\boldsymbol{\alpha}_1-\boldsymbol{\alpha}_2)J]\right\}\psi\right)dV_2=\int(\psi^*[J-Q]\psi)dV_2. \quad (16.7)$$

Since dV_1dt is Lorentz invariant, so is Eq. (15). The use of products $\varphi\chi$ for ψ corresponds to small accelerations. Reducing Eqs. (16.1), (16.3) it is found that if

$$\{E+J+c\boldsymbol{\alpha}_1\mathbf{p}_1+c\boldsymbol{\alpha}_2\mathbf{p}_2+(\beta_1+\beta_2)Mc^2\}\psi=0, \quad (17)$$

then the so-called "large" components of ψ satisfy an equation of the Pauli type. This equation contains a non-Hermitean operator and is of the form

$$E\Psi+\frac{1}{4M^2c^2}[\mathbf{p}_1J\mathbf{p}_1-p_1^2J + \mathbf{p}_2J\mathbf{p}_2-p_2^2J]\Psi+\cdots=0,$$

all other terms containing only Hermitean operators. The occurrence of a non-Hermitean part is analogous to that already encountered in Eq. (8). Analogously to Eqs. (8′), (9) it is convenient to transform the wave function by

$$\Psi^{(1)}=\Psi+(p_1^2+p_2^2)\Psi/8M^2c^2 \quad (17.1)$$

so as to have the density represented by $(\Psi^{(1)*}\Psi^{(1)})$. The two-component wave function $\Psi^{(1)}$ satisfies

$$\left\{E-2Mc^2+J+\frac{h^2\Delta J}{4M^2c^2}+\sum_{i=1}^{2}\left[-\frac{p_i^2}{2M}+\frac{p_i^4}{8M^3c^2} + \frac{h}{4M^2c^2}([\nabla_iJ\times\mathbf{p}_i]\boldsymbol{\sigma}_i)\right]\right\}\Psi^{(1)}=0. \quad (17')$$

$$(\Delta J=\Delta_1J=\Delta_2J).$$

This equation does not take into account Q and represents only the result of using Eq. (17). The expression for Q given by Eq. (16.3) is a generalization of a similar term[2] in the energy for electromagnetic interactions between point charges. In the latter case $J=\pm e^2/r$ and the term in Q represents the combined effect of the magnetic energy and the retardation in the electrostatic potential. The term in Q has to be handled with circumspection because it represents the last term of an expansion. It is known[12] in the electromagnetic case that that this term is only good for first-order calculations of the energy and that such calculations lead to sensible results using directly Eq. (16.1) and regarding it as a perturbed Eq. (17). It may, therefore, be expected that the same procedure applies to the Q of Eq. (16.3). The result of the calculation may be expressed in terms of the Pauli function $\Psi^{(1)}$. If

$$\int\psi_{\mu\nu}^*Y_{\mu\nu;\ \mu'\nu'}\psi_{\mu'\nu'}d\tau = \int\Psi^{(1)*}_{\alpha\beta}Y^P_{\alpha\beta;\ \alpha'\beta'}\Psi^{(1)}_{\alpha'\beta'}d\tau \quad (17.2)$$

$$(\mu,\nu,\mu',\nu')=1,2,3,4;\ (\alpha,\beta,\alpha',\beta')=3,4$$

then the operator Y^P may be called the *equivalent Pauli operator*. Using it with the Pauli function in first-order energy calculations is equivalent to using Y with the Dirac functions satisfying Eq. (17). Since the two parts of Q entering Eq. (16.3) occur also in other possible equations, their equivalent Pauli operators are given separately:

$$[\tfrac{1}{2}(\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2)J]^P=\frac{1}{8M^2c^2}\left\{4J\mathbf{p}_1\mathbf{p}_2+\frac{2h}{i}f\mathbf{r}(\mathbf{p}_2-\mathbf{p}_1)+h^2(3-2\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)f+h^2[r^2-r^2\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2+(\mathbf{r}\boldsymbol{\sigma}_1)(\mathbf{r}\boldsymbol{\sigma}_2)]\frac{df}{rdr} + 2hf([\mathbf{r}\times\mathbf{p}_2]\boldsymbol{\sigma}_1-[\mathbf{r}\times\mathbf{p}_1]\boldsymbol{\sigma}_2)\right\}, \quad (17.3)$$

$$\left[-\tfrac{1}{2}(\boldsymbol{\alpha}_1\mathbf{r})(\boldsymbol{\alpha}_2\mathbf{r})\frac{dJ}{rdr}\right]^P=-\frac{1}{8M^2c^2}\left\{4fx^ax^bp_1{}^ap_2{}^b+\frac{8h}{i}f\mathbf{r}(\mathbf{p}_2-\mathbf{p}_1)+\frac{2h}{i}\frac{rdf}{dr}\mathbf{r}(\mathbf{p}_2-\mathbf{p}_1) - 2hf([\mathbf{r}\times\mathbf{p}_2]\boldsymbol{\sigma}_1-[\mathbf{r}\times\mathbf{p}_1]\boldsymbol{\sigma}_2)+h^2f(12+2\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2) + h^2r^3\frac{d}{dr}\left(\frac{df}{rdr}\right)+h^2\frac{df}{rdr}[9r^2+r^2\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2-(\mathbf{r}\boldsymbol{\sigma}_1)(\mathbf{r}\boldsymbol{\sigma}_2)]\right\}, \quad (17.4)$$

where $$f=dJ/rdr, \quad \mathbf{r}=\mathbf{r}_1-\mathbf{r}_2=(x^1,x^2,x^3). \quad (17.5)$$

A short calculation shows that the operators of Eqs. (17.3) and (17.4) are Hermitean. The above

expressions can be expressed more elegantly by means of symmetrical formulas involving J, $\mathbf{p}_1$, $\mathbf{p}_2$, $(\mathbf{p}_1\mathbf{r})$, etc. It was thought, however, to be more useful to give the expressions in the above form because the occurrence of $\mathbf{p}_1$, $\mathbf{p}_2$ only on the right, uniquely defines the expressions. Combining Eqs. (17′), (17.3), (17.4) one has as an equivalent Pauli equation in $\Psi^{(1)}$,

$$\left\{-E+2Mc^2-J+\frac{p_1^2+p_2^2}{2M}-\frac{p_1^4+p_2^4}{8M^3c^2}+\frac{hf}{4M^2c^2}([\mathbf{r}\times(2\mathbf{p}_2-\mathbf{p}_1)]\boldsymbol{\sigma}_1-[\mathbf{r}\times(2\mathbf{p}_1-\mathbf{p}_2)]\boldsymbol{\sigma}_2)+\frac{J}{2M^2c^2}\right.$$
$$\times\mathbf{p}_1\mathbf{p}_2-\frac{f}{2M^2c^2}x^ax^bp_1{}^ap_2{}^b-\frac{3hf}{4iM^2c^2}\mathbf{r}(\mathbf{p}_2-\mathbf{p}_1)-\frac{h}{4iM^2c^2}\frac{rdf}{dr}\mathbf{r}(\mathbf{p}_2-\mathbf{p}_1)-\frac{h^2f}{8M^2c^2}$$
$$\left.\times(15+4\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)-\frac{h^2}{4M^2c^2}\frac{df}{rdr}[5r^2+r^2\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2-(\mathbf{r}\boldsymbol{\sigma}_1)(\mathbf{r}\boldsymbol{\sigma}_2)]-\frac{h^2r^2}{8M^2c^2}\frac{d}{dr}\left(\frac{df}{rdr}\right)\right\}\Psi^{(1)}=0. \quad (17.6)$$

For $J=-e^2/r$ this equation simplifies into Eq. (48) of reference 13. In that case terms in $\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2$, $(\boldsymbol{\sigma}_1\mathbf{r})(\boldsymbol{\sigma}_2\mathbf{r})$ combine to give a contribution to the energy

$$(he/2Mc)^2[\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2r^{-3}-3(\mathbf{r}\boldsymbol{\sigma}_1)(\mathbf{r}\boldsymbol{\sigma}_2)r^{-5}], \quad (17.7)$$

which represents the magnetic interaction energy between spins having each a magnetic moment $he/2Mc$. The interaction energy of Eq. (17.7) vanishes to the first order for the deuteron. On the other hand[14] Eq. (17.6) contains terms which do not vanish for the S states of the deuteron and give a net effect in $\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2$ of amount

$$-(h^2/6M^2c^2)(\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)\Delta J \quad (\mathrm{H}^2). \quad (17.8)$$

This interaction gives different energies in the singlet and triplet states, which corresponds to experience. The sign of Eq. (17.8) is such that for simple attractive potentials varying smoothly and monotonically with r, the energy is higher for triplets than for singlets. Thus ordinary, non-exchange, purely attractive interaction energies of the type of Eqs. (16.1), (16.3) are not likely to correspond to experience even though they contain a spin-spin dependence of the interaction energy. A repulsion in the region of smaller r produces a reversal of the sign of the effect of the expression (17.8). It is conceivable that such an interaction corresponds to reality, particularly since a combination of repulsions at small distances with attractions at larger distances is helpful for securing stability of heavy nuclei without the aid of exchange forces.

The presence of terms in $\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2$ and $(\boldsymbol{\sigma}_1\mathbf{r})(\boldsymbol{\sigma}_2\mathbf{r})$ is secured above through the introduction of the form (16.3) and not directly through the requirements of invariances. A form such as that of Eq. (17.6) remains invariant if arbitrary terms in spin-spin interactions are added to the left side, provided these terms are of order v^2/c^2. There is thus nothing binding about (17.8). The only argument advanced here is that of the attractiveness of using a simple Diracian form such as that of Eq. (16.3). The verification of invariance given by Eqs. (16.4) to (16.7) is now seen to contain little more than a direct inspection of Eq. (17.6) and its comparison with possible spin-orbit interactions of Eq. (15.7) as well as possible classical forms given by Eq. (13.2). It will thus not be necessary to go through a formal proof in discussing Diracian forms.

The use of Eq. (16.2) is somewhat analogous to that of Eq. (10). It should be noted, however, that the term in $\beta_1\beta_2J$ without Q does not give an invariant contribution to the Lagrangian.[15] This can be verified either in the Dirac or the Pauli form.

Reducing Eq. (16.2) with $Q=0$ to the Pauli form one finds

$$\left\{E-2Mc^2+J+\sum_{i=1}^{2}\left[-\frac{p_i^2}{2M}+\frac{p_i^4}{8M^2c^2}\right.\right.$$
$$-\frac{p_i^2J+2\mathbf{p}_iJ\mathbf{p}_i+Jp_i^2}{8M^2c^2}$$
$$\left.\left.+\frac{h}{4M^2c^2}[\mathbf{p}_i\times\nabla_iJ]\boldsymbol{\sigma}_i\right]\right\}\Psi^{(1)}=0. \quad (18)$$

Comparison with Eq. (15.4) shows that the spin-orbit interaction is given correctly by Eq. (18),

Comparison with Eq. (13.2) shows that the sum of the coefficients of $\mathbf{p}_1^2 J$, $\mathbf{p}_1 J \mathbf{p}_1$, $J\mathbf{p}_1^2$ is twice what it should be. The equation can be corrected for invariance either by arbitrarily modifying these terms or by looking for Diracian forms which will automatically give a correct behavior. By means of Eqs. (17.3), (17.4) such forms can be reduced to equations of the Pauli type.

It was seen that the classical Eq. (14.2) has a simpler physical interpretation than Eq. (14.1). A Diracian form agreeing with Eq. (14.2) in the sense of the correspondence principle is

$$\{E+c(\boldsymbol{\alpha}_1\mathbf{p}_1)+c(\boldsymbol{\alpha}_2\mathbf{p}_2)+(\beta_1+\beta_2)Mc^2+\beta_1\beta_2 J + \tfrac{1}{2}(\boldsymbol{\alpha}_1\boldsymbol{\alpha}_2)J+\tfrac{1}{2}(\boldsymbol{\alpha}_1\mathbf{r})(\boldsymbol{\alpha}_2\mathbf{r})(dJ/rdr)\}\psi=0. \quad (18.1)$$

Its equivalent Pauli form is found to be, by means of Eqs. (18), (17.3), (17.4), (17.5),

$$\Big\{-E+2Mc^2-J+\sum_{i=1}^{2}\Big[\frac{p_i^2}{2M}-\frac{p_i^4}{8M^3c^2}+\frac{p_i^2J+2\mathbf{p}_iJ\mathbf{p}_i+Jp_i^2}{8M^2c^2}+\frac{\hbar}{4M^2c^2}[\boldsymbol{\nabla}_iJ\times\mathbf{p}_i]\boldsymbol{\sigma}_i]-\frac{J}{2M^2c^2}(\mathbf{p}_1\mathbf{p}_2)$$

$$-\frac{f}{2M^2c^2}x^ax^bp_1{}^ap_2{}^b-\frac{\hbar}{4iM^2c^2}\Big(5f+\frac{rdf}{dr}\Big)\mathbf{r}(\mathbf{p}_2-\mathbf{p}_1)-\frac{\hbar^2}{8M^2c^2}\Big[15f+10\frac{rdf}{dr}+\frac{r^2d}{dr}\Big(\frac{df}{rdr}\Big)\Big]\Big\}\Psi^{(1)}=0. \quad (18.2)$$

Here the spin-orbit interactions are entirely of the Thomas type and there are no spin-spin interactions. Thus Eq. (18.1) may be looked at as a generalization of Eq. (10). It represents an interaction in which particle 2 is moving approximately in the field of a scalar due to particle 1. Eqs. (17.3), (17.4), (17.6), (18.2) apply only to interactions of a nonexchange type.

4. Applications

According to Rumbaugh and Hafstad[16] there is a level of Li^7 at about 400 kv above the normal level. This level is probably the $^2P_{\frac{1}{2}}$ part of the ^2P normal level of Li^7. According to Hafstad and Tuve[17] the resonance of the reaction $C^{12}+H^1\rightarrow N^{13}+h\nu$ shows indications of fine structure of the order of 80 kv. According to Herb, Parkinson and Kerst[18] there are indications of fine structure in the resonances for γ-ray production of Li, B, F, Al, Na, Be when these elements are bombarded by protons. The order of magnitude of the difference between adjacent resonance levels is about 200 kv. The spin-orbit interactions must be arranged so as to account for this order of magnitude. Using ordinary interaction potentials the order of magnitude of the expected splitting of a single particle moving in a p orbit is

$$\Delta E=-\frac{3\hbar^2}{4M^2c^2}\Big[\frac{dJ_{eff}}{rdr}\Big]_{av}\cong-\frac{\hbar^2}{M^2c^2r_0{}^2}[J_{eff}]_{av}, \quad (19)$$

where the subscript av indicates the average value. Here J_{eff} is the effective value of the interaction energy due to all the other particles considered as producing an effective central field. The nuclear radius is r_0. For $[J_{eff}]_{av}=10$ Mev and $r_0=e^2/mc^2$ the expected ΔE is then of the order of 50 kv. This agrees with the observations on N^{13} but is too small for the 400 kv splitting in Li^7. These are fitted better with $[J_{eff}]_{av}=20$ Mev, $r_0=e^2/2mc^2$ which is not unreasonable. Eq. (19) corresponds to the use of Eq. (15.4) with $b=1$, because in such a case the spin-orbit interaction consists entirely of terms of type

$$[\boldsymbol{\nabla}_i\sum_{j\neq i}J_{ij}\times\boldsymbol{\sigma}_i]\mathbf{p}_i \quad \text{and} \quad \sum_{j\neq i}J_{ij}$$

gives directly the potential in which particle i is moving. Thus Wigner forces are readily reconcilable with present experimental indications as to the magnitude of fine structure using essentially interactions of the type of Eq. (18.1). The inversion of the fine structure in Li^7 is also in agreement with this type of interaction energy.

For Majorana forces Eq. (15.7) with $a=1$ gives an interaction which is somewhat analogous to the Wigner case, just discussed, as is seen from Eq. (15.8′). With this form the following contributions to the fine structure are found for a proton interacting with a complete shell of $2(2L'+1)$ neutrons

$$\Delta E=-\frac{(2L+1)(2L'+1)\hbar^2}{32\pi^2M^2c^2L(L+1)}\int\{L(L+1)\cos\theta$$
$$\times P_L[3Q_1Q_2+r_1Q_1'Q_2+r_2Q_1Q_2']$$
$$+\sin^2\theta P_L'[(4+L(L+1))Q_1Q_2+2r_1Q_1'Q_2$$
$$+2r_2Q_1Q_2'+r_1r_2Q_1'Q_2']\}$$
$$\times R_{L'}(1)R_{L'}(2)P_{L'}J_{12}d\tau_1d\tau_2. \quad (19.1)$$

Here L = azimuthal quantum number of proton; L' = azimuthal quantum number of complete shell; P_L = Legendre function of argument $\cos\theta$, where θ is the angle between the directions of points 1 and 2; $R_{L'}$, rQ are the radial functions of proton and neutron respectively. Derivatives with respect to r and $\cos\theta$ are indicated by $'$. The normalization is such that

$$\int R_L^2r^2dr=1; \quad \int Q^2r^4dr=1. \quad (19.2)$$

Eq. (19.1) applies only to cases in which a proton is outside a complete shell. It does not take care of perturbations due to other states of the shell, which, according to Feenberg and Wigner,[19] are important in nuclear structure. The effect of such perturbations is not taken into account in this paper.

For Li^7 estimates of expected fine structure can be made by supposing that there are two protons in s states and one proton in a p state. Two neutrons are supposed to be in s states and two in p states. The pairs of like particles in s states form complete shells. Their effect can be computed by means of Eq. (19.1). The two neutrons in p states are considered here to be coupled into a ^1S term. They effectively form a complete shell of two particles. Eq. (19.1) applies to their effect on ΔE, provided the result of the calculation is divided by $6/2=3$. This can be verified by explicit calculation. In addition there is an interchange effect due to the fact that the proton in the p state is a particle identical with the two protons in the s shell. In the estimates, the radial wave functions of all particles with the same L were taken to be the same, independently of whether they are protons or neutrons. The radial functions used were such that

$$R_0=N_Re^{-\mu r^2/2}, \quad N_R^2=4\mu^{3/2}/\pi^{1/2};$$
$$Q=N_Qe^{-\nu r^2/2}, \quad N_Q^2=8\nu^{5/2}/3\pi^{1/2}; \quad (19.3)$$

and the interaction potential was taken to be

$$J=Ae^{-\alpha r^2}. \quad (19.4)$$

The contributions to ΔE were found to be:

$$(\Delta E)_{ss}=-\frac{3\hbar^2}{4M^2c^2}\frac{A(\mu\nu)^{5/2}(\mu+4\alpha)}{[\alpha(\mu+\nu)+(\mu+\nu)^2/4]^{5/2}} \quad (19.5)$$

due to the s shell of neutrons,

$$(\Delta E)_{sp}=(\Delta E)_{ss}-\frac{3\hbar^2}{2M^2c^2}\frac{A(\mu\nu)^{5/2}\alpha}{[\alpha(\mu+\nu)+\mu\nu]^{5/2}} \quad (19.6)$$

due to the s shell of protons, and

$$(\Delta E)_{pp}=-\frac{\hbar^2}{4M^2c^2}\frac{A\alpha\nu^5(4\alpha\nu-3\nu^2)}{[2\alpha\nu+\nu^2]^{7/2}} \quad (19.7)$$

due to two p neutrons in a ^1S configuration.

Using $A=38\ mc^2$, $\alpha=16\ Mmc^2/\hbar^2$, and trying to fit the apparent experimental value $\Delta E=-0.8\ mc^2$, one obtains approximate agreement using $\mu=\nu\leqq 40\ Mmc^2/\hbar^2$. No precise fit was attempted. The above values of μ and ν correspond to values of $(r^2)_{av}^{\frac{1}{2}}$ of 1.7×10^{-13} cm and 2.2×10^{-13} cm for s and p particles, respectively. The maximum in the number of p particles per unit thickness of a thin spherical shell (per $\Delta r=1$) would be at 2.0×10^{-13} cm. Since the calculation is not precise, these numbers may be considered satisfactory. It may be premature to expect an exact agreement inasmuch as even in atoms calculations of fine structure using Hartree and Fock fields do not always give correct results.

The values of μ and ν are seen to agree quite well with the calculations of Feenberg and Wigner,[19] who obtain from mass defect values of $\mu=\nu=2\alpha\sigma$ of 26 and 32 in units $Mmc^2/\hbar^2$. Increasing the value of A from $38mc^2$ to $63mc^2$ the value of $\mu=\nu$, as estimated from fine structure of Li^7, drops to $27Mmc^2/\hbar^2$. The agreement thus obtained may be partly accidental.

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11. W. Heisenberg and W. Pauli, Zeits. f. Physik **56**, 1 (1929); **59**, 168 (1930); E. Fermi, Rendiconti d. R. Acc. dei Lincei (6) **9**, 1 part, p. 881 (1929); P. A. M. Dirac, Proc. Roy. Soc. **A136**, 453 (1932); P. A. M. Dirac, V. Fock, B. Podolsky, Physik. Zeits. Sowjetunion **2**, 468 (1932).
12. G. Breit, Phys. Rev. **39**, 616 (1932).
13. Second reference of footnote 2.
14. Bethe and Bacher, Rev. Mod. Phys. **8**, 113, Eq. (46), (1936). It has been pointed out by Casimir [Physica **3**, 936 (1936)] that the physical conclusion about the smallness of the $^1S-{}^3S$ energy difference arrived at by Bethe and Bacher is not correct. Instead, Casimir calculates the magnetic interaction of the currents due to the spins. There is an apparent contradiction between using Eq. (17.7) and Casimir's calculation. This contradiction is only apparent, as is well known in the theory of hyperfine structure, and it does not arise if Eq. (17.6) is used. It is clear from Eq. (17.8) that if $J=e^2/r$ the first-order perturbation energy of the expression (17.8) does not vanish but is indeterminate. Its value can be defined modifying the function $1/r$ into $1/\rho$, where $1/\rho$ is the solution of Poisson's equation subject to standard boundary conditions at infinity and corresponding to a very concentrated but a finite charge density close to $r^2=x^2+y^2+z^2=0$, having total space integral $=1$. In the limit of infinite concentration of charge density $\Delta(1/\rho)\rightarrow-4\pi\delta(x, y, z)$. In this limit the perturbation energy to Eq. (17.8) becomes

$$\Delta E=\frac{8\pi}{3}\left(\frac{e\hbar}{2Mc}\right)^2\psi^2(0)[2s(s+1)-3],$$

where $s=1$ for ^3S, $s=0$ for ^1S, and $\psi(0)$ is the Schroedinger wave function representing the relative motion of proton and neutron taken at $r=0$. This formula agrees with Casimir's who obtains the same result multiplied by $\gamma_n\gamma_p/4$. Casimir's γ's are defined so that the projection of the magnetic moment on an axis is $(\gamma/2)(e\hbar/2Mc)$ when the projection of the spin is $\hbar/2$. For particles obeying Dirac's equation $\gamma/2=1$ and the factor $\gamma_n\gamma_p/4$ should thus be absent in our discussion. From Eq. (17.6), collecting and rearranging terms responsible for spin-spin interactions, one obtains as perturbation energy

$$\Delta E=\frac{\hbar^2 f}{4M^2c^2}[(\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)-3r^{-2}(\mathbf{r}\boldsymbol{\sigma}_1)(\mathbf{r}\boldsymbol{\sigma}_2)]$$
$$-\frac{\hbar^2\Delta J}{4M^2c^2}[(\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)-r^{-2}(\mathbf{r}\boldsymbol{\sigma}_1)(\mathbf{r}\boldsymbol{\sigma}_2)],$$

which shows clearly how the first part alone is inadequate for a general treatment. This last expression for ΔE can be compared with analogous expressions in the theory of hyperfine structure as, e.g., Eq. (2) in G. Breit, Phys. Rev. **37**, 51 (1931). The inclusion of Casimir's factor γ corrects for the fact that the actual magnetic moment differs from that predicted by Dirac's equation. On the other hand the possible effect of ΔJ, where J stands for the interaction energy between proton and neutron, is not included in his treatment. If Eq. (17.6) were applicable to the interaction between an electron and a neutron (or proton) one would expect a coupling of the electron to the nucleus of a nonelectromagnetic origin. The present agreement of values for the magnetic moment of the deuteron and other nuclei as obtained by different methods (Stern-Rabi) indicates that this coupling is not large. An ultimate decision must, however, be postponed until present experimental uncertainties are cleared up. Since the additional interactions discussed here would not be expected to vary in the same way with distance as for ordinary magnetic effects it may also be possible to test for their presence by a careful comparison of hyperfine structure in spectroscopic terms having different azimuthal quantum numbers.

15. C. F. v. Weizsäcker, Zeits. f. Physik **102**, 572 (1936). von Weizsäcker recently arrived at Eq. (16.1) with $Q=0$ from considerations of Fermi's theory of β-ray activity and Heisenberg's idea of accounting for nuclear interactions on the basis of this theory. The reduction of Eq. (16.1) to the Pauli form made by von Weizsäcker agrees with the one given here except for one detail: the equation obtained here for $\Psi^{(1)}$ is the same as that obtained by von Weizsäcker for Ψ. One would expect that a complete calculation with a relativistic scheme such as Fermi's will lead to a relativistic approximation to the order v^3/c^3. A complete calculation, however, using Fermi's theory is impossible at present on account of its divergence. The cutting off of the integrals introduces a nonrelativistic feature in such calculations. The fact that von Weizsäcker obtains $Q=0$ may be attributed to this cause. The calculation of von Weizsäcker is more nearly analogous to that of all the terms to the first order in e^2/r [G. Breit, Phys. Rev. **34**, 553 (1929), pp. 566–572; H. Bethe and E. Fermi, Zeits. f. Physik **77**, 296 (1932); see also last reference of footnote 11] than to the procedure of first eliminating the electrostatic field and then introducing spin corrections. One may, therefore, expect his result to apply better to the discussion of collisions by Born's method rather than to the calculation of binding energies. Eq. (16.2) with $Q=0$ gives, in fact, a relativistically invariant description of collisions for J having an infinitely small range and for small collision cross sections. It is thus analogous to Møller's form in the electromagnetic case.

16. L. H. Rumbaugh and L. R. Hafstad, Phys. Rev. **50**, 681 (1936).

17. L. R. Hafstad, N. P. Heydenburg and M. A. Tuve, Phys. Rev. **50**, 504 (1936); G. Breit and F. L. Yost, Phys. Rev. **48**, 204 (1935). The estimate of fine structure given on p. 210 of this paper was too small.

18. R. G. Herb, D. W. Kerst and J. L. McKibben, Bull. Am. Phys. Soc. Chicago Meeting, Paper 12; Phys. Rev. **51**, 59 (1937).

19. E. Feenberg and E. Wigner, Phys. Rev. **51**, 95 (1937). The writer is very grateful to the authors for informing him of their results before publication. H. Bethe and M. E. Rose [Cornell conference on nuclear physics] reported similar conclusions regarding the effect of the ^1D state of the p^2 configuration of neutrons.

Ionization and Dissociation of Polyatomic Molecules by Electron Impact. I. Methane[1]

LINCOLN G. SMITH
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey
(Received December 7, 1936)

The first of a series of mass-spectrograph studies of the products of ionization of polyatomic molecules by low speed electrons is described. The following are the positive ions detected in methane together with their appearance potentials in volts: CH_4^+ (13.1±0.4); CH_3^+ (14.4±0.4); CH_2^+ (15.7±0.5, 22.9±0.8); CH^+ (23.3±0.6); C^+ (26.7±0.7); H^+ (22.7±0.5, 29.4±0.6); H_2^+ (27.9±0.5); and H_3^+ (25.3±1.0). The following negative ions were also observed: CH_2^-; CH^-; C^-; and H^-. From the higher appearance potential of H^+ and the appearance potentials of C^+ and C^- three independent upper limits are calculated for the heat of dissociation of CH_4 to normal atoms which lead, respectively, to the following three upper limits for the heat of sublimation of carbon: $L(C) \leq 6.1 \pm 0.6$ volts or 141±14 kcal.; $L(C) \leq 5.7 \pm 0.7$ volts or 131±16 kcal.; $L(C) \leq 6.0 \pm 0.9$ volts or 139±21 kcal. Thus of the three values of $L(C)$ recently proposed from data on predissociation in CO, these results are inconsistent with the value $L(C) = 168.8$ kcal. but are quite consistent with the value $L(C) = 123.6$ kcal. Correlations of known ionization energies with the best obtainable data on the relative energies of the possible stable states of a carbon and four hydrogen atoms give reasonable interpretations of all observed appearance potentials. Upper limits for the ionization potentials of CH_3, CH_2, and CH are deduced. These are: $I(CH_3) \leq 9.9$ volts; $I(CH_2) \leq 12.0$ volts; $I(CH) \leq 11.7$ or 16.2 volts. Two general conclusions are drawn. The first is that most ions are only formed when the parent molecules are broken into as many parts as possible. The second is that interpretations of all but four appearance potentials are possible on the assumption that the total excitational and kinetic energy of products formed in an electron impact from a CH_4 molecule be less than two volts.

INTRODUCTION

ONE of the important physical tools for studying molecular structure is the mass spectrograph wherein ions are formed by impacts of electrons of known energy with molecules. With this instrument one can determine in most cases what ions are produced from molecules of a particular variety through approximate measurements of the mass-to-charge ratios of the ions. Also, one can determine for ions of each kind: the relative probabilities for formation under different conditions in the ion source; the appearance potential or the minimum energy required to produce them; and, possibly, the kinetic energies with which they are formed. The first two types of information are of interest chiefly in themselves and can seldom be compared with results obtained by other means either experimental or theoretical. The appearance potential of undissociated ions or the ionization potential of the molecule under investigation is also important *per se* and often checks or supplements spectroscopic or theoretical results. Interest in the appearance potentials and kinetic energies of other ions lies not so much in the quantities measured as in the dissociation and ionization energies which can in some cases be calculated therefrom by use of data from other scources. Since these ionization and dissociation energies comprise the most important contributions of a mass spectrograph to the field of molecular structure, a brief review of how they are obtained and of the chief sources of uncertainty involved in their calculations will probably not be out of place here.

The appearance potential of an ion which lacks one or more of the atoms of the parent molecule is the sum of three quantities: a dissociation energy; an ionization energy; and the total minimum excitational and mutual kinetic energy with which the products can dissociate. (The ionization energy in the case of a negative ion is an electron affinity—with negative sign—and if both a positive and a negative ion are produced, it is the algebraic sum of an ionization energy and an electron affinity.) Provided one knew what all the products of dissociation are, how much kinetic energy each has, and in what excited state each is formed, he could calculate the dissociation energy from the appearance potential and a knowledge of the ionization energy or *vice versa*.

[1] The results on positive ions formed in methane were discussed briefly in a paper by W. Bleakney, E. U. Condon and L. G. Smith which was presented at the Symposium on Molecular Structure held at Princeton, N. J. under the auspices of the American Chemical Society (Dec. 31, 1936–Jan. 2, 1937) and which has been published in the Journal of Physical Chemistry.

Unfortunately, if more than one atom of the parent molecule is missing in the ion, there are at least two possibilities for the states of aggregation of the missing atoms, and the reaction occurring can only be determined through considerations of energy relations. Furthermore, the kinetic energies of unionized products of dissociation cannot be calculated from that of the ion if more than one of the former is produced from a molecule. Finally, *a priori* knowledge of the states of excitation of the products is never at hand. Conclusions drawn from combinations with other data of the appearance potential and kinetic energy of an atomic ion formed from a diatomic molecule are subject only to uncertainties in the electronic states of the products of dissociation. In the case of the appearance potential of an ion lacking but one of the atoms of a parent polyatomic molecule, conclusions are also subject to uncertainties with regard to vibrational energy of the ion. In general, where there are more than two products of dissociation of a single molecule, not only electronic and vibrational energy but kinetic energies of the products as well as their states of aggregation are uncertain. Here the best one can hope to do is to determine the reaction occurring and from this to determine a value of either the dissociation or the ionization energy involved plus the total excitational and kinetic energy of the products. It is evident that such a value is an upper limit for the true dissociation or ionization energy (or a lower limit for the true electron affinity). Additional factors complicating the interpretation of results obtained by the electron impact method are: experimental errors in these results (which are seldom less than 1 percent and often as high as 4 or 5 percent); and uncertainties in quantities obtained from other sources. The latter uncertainties, however, add importance to any conclusions which may be drawn even if it is possible to determine only upper or lower limits for the true values.

The results for diatomic molecules obtained by the electron impact method have in many cases corroborated and supplemented spectroscopic and thermochemical data. Also they have given experimental evidence in support of the Franck-Condon principle and the repulsive electronic states of such molecules predicted by quantum mechanics. Results for the triatomic molecules that have been studied (H_2O, H_2S, N_2O, NO_2, SO_2, CO_2 and CS_2) have also in some cases checked and added to thermochemical and spectroscopic data. However, little attempt has been made to interpret in the light of other data results for the more complex molecules which have been studied (NH_3, C_2N_2, CH_4, CH_3Cl, C_3H_8, C_4H_{10}, C_5H_{12}, C_2H_2, C_6H_6). Good reviews of all this work have been prepared by Smyth,[2] and more recently by de Groot and Penning,[3] and by Sponer.[4]

The mass spectrograph analysis of methane, results of which are reported in this paper, is the first of a series of such analyses to be undertaken in this laboratory. The results for methane yield some information regarding unknown and uncertain quantities. It is to be hoped that with the accumulation of further data for other molecules more such information will be obtained.

Apparatus and Procedure

The mass spectrograph used to study ionization processes in methane is of the type described by Bleakney[5] and by Tate, Smith, and Vaughan.[6] A detailed description of the instrument, the gas-handling system, the electrometer-tube amplifier used to measure the ion current, and the device for recording automatically this current as a function of the potential applied to accelerate either the ions or the electrons will be found in a recent paper.[7]

Fig. 1 shows a typical mass spectrum obtained with the automatic recorder of the positive ions with m/e values from 12 to 16 formed in methane by electrons with an energy of 50 electron volts. When this record was obtained the magnetic field was kept constant at about 550 gauss (as in all work on methane), and the potential applied to the electron gun was fixed at 50 volts, while a variable potential accelerating the ions was applied by the drum potentiometer which is a

[2] H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931).
[3] de Groot and Penning, *Handbuch der Physik*, Vol. 23/1 (J. Springer, Berlin, 1933).
[4] H. Sponer, *Molekulspektren* (J. Springer, Berlin, 1935, 1936).
[5] W. Bleakney, Phys. Rev. **40**, 496 (1932).
[6] J. T. Tate, P. T. Smith, and A. L. Vaughan, Phys. Rev. **48**, 575 (1935).
[7] W. W. Lozier, P. T. Smith, L. G. Smith, and W. Bleakney, Rev. Sci. Inst. **8**, 51 (1937).

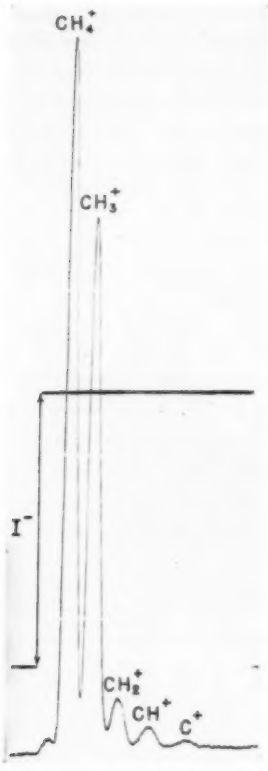


FIG. 1. Mass spectrum of the heavier positive ions formed in methane. Ordinates represent ion currents and abscissae analyzer voltage or e/m values. I^- is the electron current recorded simultaneously with the ion current. The small peak to the left of the CH_4^+ peak corresponds to ions with $m/e=17$ which can only be $C^{13}H_4^+$ ions. The ratio of the heights of these two peaks is $\sim 1/100$ which is approximately the abundance ratio C^{13}/C^{12}.

part of the recorder. The height of a peak is assumed to be proportional to the intensity of the corresponding ionization or number of ions of the given kind formed per second per unit volume.[8] The pressure of methane in the mass spectrograph when Fig. 1 was obtained was $\sim 4\times 10^{-5}$ mm of Hg.[9]

[8] The deflection of the galvanometer is strictly proportional to the ion current arriving at the collector. This fact coupled with the fact that peaks for ions with m/e as high as 6 are flat topped indicates that even for ions with $m/e=16$ this assumption should not be far from the truth.

[9] Pressures were estimated by calculation from the absolute values of electron and total positive ion currents, the geometry of the ion source, and the value given by J. T. Tate and P. T. Smith (Phys. Rev. **39**, 270 (1932)) for the cross section of common gas molecules for ionization which was assumed to be correct for methane. Such estimates of pressures should not be in error by more than factors of two.

Fig. 2 illustrates the method of determining the appearance potential of an ion (in this case H^+ formed from CH_4). Curve 1 was taken with the ion-accelerating potential fixed so that H^+ ions passed through the exit slit of the analyzer and with the variable potential from the drum applied in series with a fixed potential to accelerate the electrons. Curve 2 was taken in similar fashion with the analyzer set to record He^+ ions formed in helium gas which was admitted into the apparatus simultaneously with the methane. The curve for He^+ serves to correct the recorded electron energies for contact potentials in the instrument. It will be observed that the upward break of curve 2 from its horizontal portion is more abrupt than that of curve 1 and that to the right of the break, curve 2 is nearly a straight line while curve 1 has considerable upward curvature.[10] Hence in de-

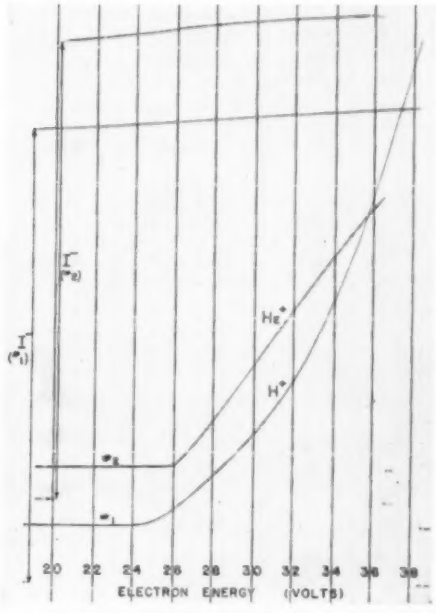


FIG. 2. Appearance potential curves for H^+ ions formed in methane and He^+ ions formed in helium. Ordinates represent ion currents. I^- is the electron current recorded in each case simultaneously with the ion current.

[10] This effect is characteristic of the appearance potential curves for all ions from methane and has been noted by others who have measured the appearance potentials of molecular ions. The effect is presumably due first to the fact that at room temperature a gaseous molecule may exist in one of a larger number of energy states than a gaseous atom. Secondly, it is due to the fact that a molecu-

termining the lowest appearance potential of H^+ ions it was not feasible to attempt to fit curves 1 and 2 together, nor could one extrapolate to zero current any linear portion of curve 1 to the right of the upward break. It seemed best in this as in all other cases to use the method of selecting the appearance potential for each ion as the lowest electron energy at which the corresponding ion current was detectable. This method is open to several objections, the chief of which is that the value obtained depends somewhat on the sensitivity used in obtaining the corresponding curve. This source of error was reduced as far as possible by adjusting the sensitivity of the amplifier and the relative pressures of methane and the calibrating gas so that in each case the curve for ions from methane had roughly the same slope to the right of its upward break as the curve for ions formed in the calibrating gas. With the total pressure of impurities about 5×10^{-8} mm of Hg, the pressures of methane used in determining the appearance potentials of positive ions ranged from about 5×10^{-6} to about 5×10^{-5} mm of Hg, while the pressure was about 1×10^{-4} mm of Hg when similar determinations were made for negative ions.[9] An equipotential, oxide-coated cathode was used in obtaining all appearance potentials. Because of the smaller range of the speeds with which electrons leave such a source, the upward breaks in curves like those of Fig. 2 were more sharply defined when

lar ion may be formed in one of a much larger number of closely spaced energy states within a range of a few volts above the lowest state.

TABLE I. *Ions formed in methane.*

Observed Ion	% of Total Ionization (Electron Energy 50 volts)	Observed Appearance Potentials (volts)	Probable Process $CH_4\rightarrow$:		Calculated Minimum Energy (volts)	Additional Energy Required or Ionization Energy Deduced (volts)
Positive ions						
H^+	3.0	22.7±0.5	H^++CH_2+H	(1)	21.6	1.1
			or H^++CH+H_2	(2)	20.6	2.1
		29.4±0.6	H^++C+3H	(3)	28.6	0.8
H_2^+ *	0.3	27.9±0.5	H_2^++C+2H	(4)	26.0	1.9
H_3^+ *	0.005	25.3±1.0	H_3^++C+H	(5)	$24.1-D(H_3^+)$	$1.2+D(H_3^+)$
			or $H_3^++CH^-$	(6)	$20.6-D(H_3^+)-E(CH)$	$4.7+D(H_3^+)+E(CH)$
C^+	0.6	26.7±0.7	C^++4H	(7)	26.3	0.4
CH^+	1.7	23.3±0.6	CH^++3H	(8)	$11.6+I(CH)$	$I(CH)\leqq11.7$
			or CH^++H_2+H	(9)	$7.1+I(CH)$	$I(CH)\leqq16.2$
CH_2^+	4.2	15.7±0.5	$CH_2^++H_2$	(10)	$3.7+I(CH_2)$	$I(CH_2)\leqq12.0$
		22.9±0.8	CH_2^++2H	(11)	$8.1+I(CH_2)$	$\leqq2.8$
CH_3^+	39.5	14.4±0.4	CH_3^++H	(12)	$4.5+I(CH_3)$	$I(CH_3)\leqq$ 9.9
CH_4^+	50.7	13.1±0.4	CH_4^+	(13)	$I(CH_4)$	$I(CH_4)=13.1$
Negative ions						
H^-	0.04	6.1±0.3	H^-+CH_3	(14)	3.8	2.3
		6.9±0.8	H^-+CH+H_2	(15)	6.4	0.5
		7.3±1.0	H^-+CH_2+H	(16)	7.4	~0
		18.0±0.6	$H^-+CH^++H_2$	(17)	$\leqq18.1$	~0
			or $H^-+CH_3^+$	(18)	$\leqq13.7$	4.3
C^-	0.003	27.4±0.6	C^-+H^++3H	(19)	26.7	0.7
CH^-	0.005	10.2±0.3	CH^-+3H	(20)	$11.6-E(CH)$	$E(CH)\geqq1.4$
		24.5±0.5	CH^-+H^++2H	(21)	$25.1-E(CH)$	$\geqq0.8$
			or $CH^-+H_3^+$	(22)	$20.6-D(H_3^+)-E(CH)$	$3.9+D(H_3^+)+E(CH)$
CH_2^-	0.002	8.9±0.3	CH_2^-+2H	(23)	$8.1-E(CH_2)$	$0.8+E(CH_2)$
		23.4±0.6	$CH_2^-+H^++H$	(24)	$21.6-E(CH_2)$	$1.8+E(CH_2)$
			or $CH_2^-+H_2^+$	(25)	$19.0-E(CH_2)$	$4.4+E(CH_2)$

* The results for H_3^+ and H_2^+ ionization in methane are of interest in connection with attempts to produce helium of mass three by bombardment of deuterium with canal rays from an intense, high voltage discharge in deuterium. (Phys. Rev. **46**, 81 (1934); Phys. Rev. **47**, 800(A) (1935).) Samples of the treated gas were allowed to stand over hot copper oxide and a liquid-air trap to remove the hydrogen in the form of water. In the residual gases admitted to the mass spectrograph later used for obtaining the present results on methane, ions were found with $m/e=3$ whose appearance potential was approximately equal to the ionization potential of He (24.5 volts). These were at first believed to be He^{3+} ions, but it was later found that the rate of diffusion through a capillary of the gas from which they were formed was smaller than that of ordinary helium. It was then suggested that the ions might be formed from some hydrocarbon gas like methane. The present results indicate: (1) that they were probably not HD^+ ions formed from deuteromethane since their appearance potential was too low; and (2) that only very few of them could have been H_3^+ ions from ordinary methane.

such a source was used than when a tungsten filament supplied the electrons.

Experimental Results

A list of all ions, both positive and negative, which were observed, their approximate relative intensities for an electron energy of 50 volts, and their appearance potentials will be found in the first three columns of Table I. The errors quoted in column three are estimated probable errors. Helium served as the calibrating gas in determining the appearance potentials of the negative ions and H^+ ions, while argon and a slight impurity of hydrogen were used in the cases of the other ions. In all cases the calibrating gas was in the instrument along with methane. No multiply charged ions could be detected at electron energies as high as 80 volts.

The positive ions were all observed when either a tungsten filament or an oxide-coated cathode, operating at considerably lower temperature, was used as an electron source. Their relative intensities were the same within experimental error in the two cases indicating that few, if any, ions were formed by ionization of products of thermal dissociation at either cathode. In Table II are given the results of three independent measurements of the relative intensities of the heavier positive ions showing the constancy of these quantities at widely different pressures and electron currents. Constancy of the relative intensities of H_3^+, H_2^+, and H^+ ionizations at different pressures is shown by Fig. 3 in which are plotted the intensities of H_3^+ and H_2^+ as functions of the intensity of CH_4^+ and the intensity of H^+ as a function of that of H_2^+. Measurements of the intensity ratios H_3^+/CH_4^+, H_2^+/CH_4^+, and H^+/CH_4^+ at electron currents ranging from 3.1 to 60, from 0.52 to 32, and from 0.52 to 60 microamperes, respectively, gave results which in no case disagreed with the ratios obtained from the curves of Fig. 3 by more than a factor of two.

Table II. *Percents of total ionization at various pressures and electron currents.*

Approximate Pressure (mm of Hg)	Electron Current (Microamp.)	CH_4^+	CH_3^+	CH_2^+	CH^+	C^+
1×10^{-6}	0.53*	52.3	39.2	3.4	1.3	0.6
4×10^{-5}	4.3*	52.0	38.8	3.8	1.6	0.6
2×10^{-6}	61.0†	49.0	41.0	4.3	1.9	0.7

* Electrons supplied by oxide-coated cathode.
† Electrons supplied by tungsten filament.

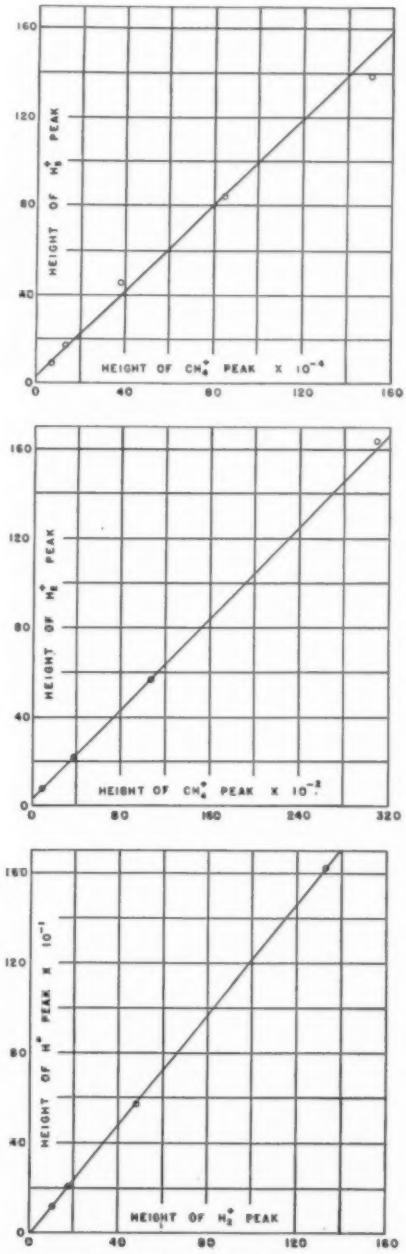
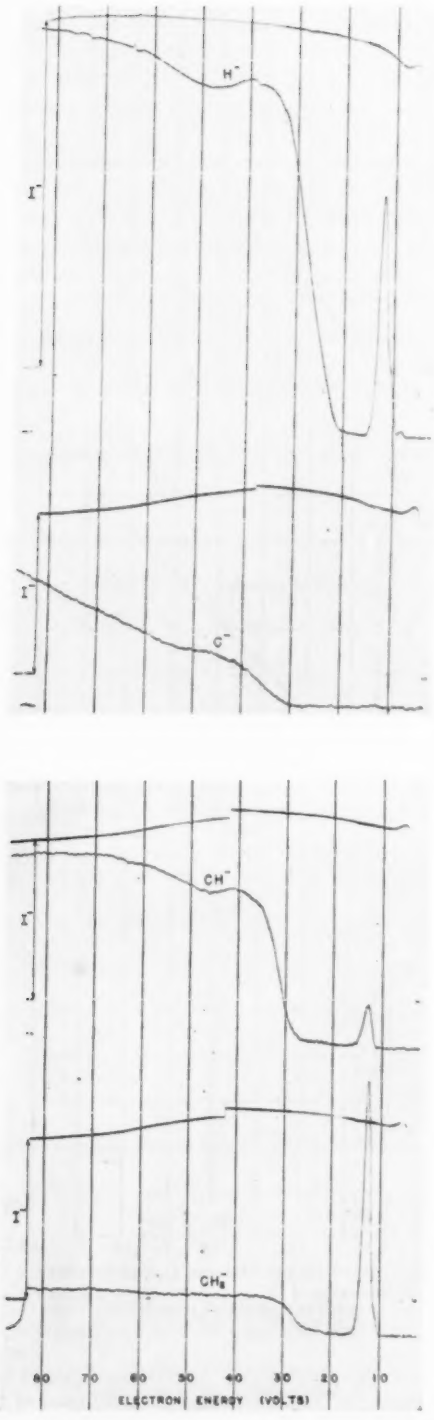


Fig. 3. Intensities of H_3^+ and H_2^+ as functions of CH_4^+ and the intensity of H^+ as a function of that of H_2^+. The linearity of these curves shows that H^+, H_2^+, and H_3^+ ions are formed from CH_4 molecules as primary products.



From all these facts we may be sure that each positive ion is formed as the result of a single impact between an electron and a CH_4 molecule.

The heights of the negative ion peaks were not measured as functions of pressure or electron current, nor were these peaks looked for when a tungsten filament was being used as a source of electrons. However, the absence of secondary processes in the formations of any of the positive ions together with the fact that the ion current *vs.* electron energy curves for all the negative ions observed in methane (Fig. 4) are of the same character as those obtained by various investigators for other negative ions which are formed in single electron impacts leads one to assume that all negative ions from CH_4 molecules are formed in the same manner.

Comparisons with Other Electron Impact Results for Methane

The ionization potential of CH_4 was measured prior to 1929 by several workers using instruments which could not separate ions according to their mass-to-charge ratios. These results are summarized in Table III. Using a mass spectrograph, Hogness and Kvalnes[11] found that when a tungsten filament supplied electrons CH_4^+, CH_3^+, CH_2^+, CH^+, C^+, H_2^+, and H^+ ions were produced in methane, but that with an oxide-coated cathode as source of electrons only CH_4^+ and CH_3^+ appeared in about equal numbers at minimum electron energies of 14.5 and 15.5 volts, respectively. They therefore ascribed the forma-

Table III. *Early results on the ionization potential of CH_4.*

Observer	Reference	Ionization Potential (Volts)
Mayer	Ann. d. Physik **45**, 1 (1914)	13.5
Hughes and Dixon	Phys. Rev. **10**, 495 (1917)	9.5
Hughes and Klein	Phys. Rev. **23**, 450 (1924)	13.9
Pietsch	Dissert. Berlin p. 534 (1926)	12.5±0.5
Glockler	J. Am. Chem. Soc. **48**, 2021 (1926)	14.4 to 15.2
Pietsch and Wilke*	Zeits. f. Physik **43**, 342 (1927)	14.58±0.05
Morris	Phys. Rev. **32**, 942 (1928)	14.4

* Pietsch and Wilke also found a second critical potential for ionization at 15.40±0.05 volts which was later interpreted by Hogness and Kvalnes, reference 11, as the appearance potential of CH_3^+.

[11] Hogness and Kvalnes, Phys. Rev. **32**, 942 (1928).

Fig. 4. Ionization efficiency curves for negative ions formed in methane. Ordinates represent ion current. I^- is the electron current recorded in each case simultaneously with the ion current. The electron energy increases from right to left.

tions of the other ions to ionization of the products of thermal dissociation at the tungsten filament. Hipple and Bleakney,[12] analyzing methane with a mass spectrograph of the same type as, but less sensitive than, that used in the present work, observed the ions CH_4^+, CH_3^+, CH_2^+, CH^+, C^+, and H^+ at the minimum electron energies 13.7, 14.7, 15.7, 23, 27 and 31 volts, respectively. Pressure, electron current, and pumping speed variations showed these all to be primary products. In addition, an H_2^+ peak was observed about 10^{-4} as high as the CH_4^+ peak.

Because of the use of lower pressures made possible by improved vacuum technique and greater sensitivity of the device for measuring ion currents, it is believed that the author's values for the appearance potentials of CH_4^+ and CH_3^+ are more reliable than those of Hogness and Kvalnes or those in Table III. All the results of Hipple and Bleakney agree within experimental error with those of the author excepting their values of the relative intensity of H_2^+ ionization and the appearance potential of H^+ ions. Evidently H^+ ionization in their apparatus was too weak to enable them to detect its appearance at 22.7 volts, and their 31−volt value probably corresponds to the author's value of 29.4 volts for the second appearance potential of H^+ ions.

The value 12.72 ± 0.05 volts for the ionization potential of CH_4 reported by Smith and Bleakney[13] was determined by a method to which several objections have been raised. The value given in Table I was obtained by the method described above.

Interpretation and Discussion

In the discussions below the following abbreviations will be used:

$A(X^+)\equiv$ Appearance potential of X^+ ions formed by electron impact in methane;
$I(X)\equiv$ Ionization potential of X;
$E(X)\equiv$ Electron affinity of X;
$D(X)\equiv$ Heat of dissociation of X to normal atoms in the gaseous state;
$Q(X)\equiv$ Energy evolved in the formation of a gram mole of X from its elements in the states in which they exist at room temperature and atmospheric pressure;
$L(C)\equiv$ Heat of sublimation of carbon (energy absorbed by a gram mole of carbon in changing from diamond to a gas consisting of atoms in the ^3P normal state).

Here X stands for the chemical symbol of a molecule, a radical, or an atom. All these quantities will correspond to reactions taking place at the absolute zero of temperature.[14] Whenever energy values have a direct bearing on thermochemical data they will be given both in volts (meaning electron volts per molecule) and in kcal. (meaning kcal. per mole). The conversion factor is: 1 volt = 23.054 kcal.

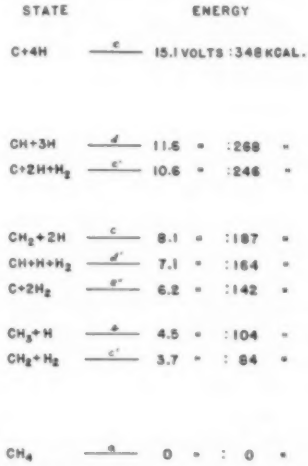


FIG. 5. Energies of the possible stable states of combination in which a carbon atom and four hydrogen atoms may exist referred to the state CH_4 as zero.

Fig. 5 shows the energies of the possible stable states of combination in which a carbon atom and four hydrogen atoms may exist, referred to the state CH_4 as zero. These energies are in accord with what seem to be the most reliable data available, though considerable uncertainty

[12] J. A. Hipple, Jr. and W. Bleakney, Phys. Rev. **47**, 802(A) (1935).
[13] L. G. Smith and W. Bleakney, Phys. Rev. **49**, 883(A) (1936).
[14] Dissociation and ionization energies obtained spectroscopically, since they involve only considerations about two energy states of a single molecule, correspond to reactions, from the standpoint of thermochemistry, at absolute zero. According to the Franck-Condon principle an electron striking a molecule cannot change directly either the translational or rotational kinetic energies of the nuclei. Hence an appearance potential determined by the electron impact method is simply the energy difference between a vibrational level of an upper electronic state and one of a lower electronic state and is thus the minimum energy required for a reaction at absolute zero.

exists as to their validity. Levels c', d', e', and e'' must lie below levels c, d, e, and e', respectively, by $D(H_2)=4.46\pm0.04$ volts or 102.9 ± 0.9 kcal.[15] The position of the level e is determined by means of the following cycle:

$$\begin{aligned} C_{diamond}+2H_2 &\rightarrow CH_4 \quad +Q(CH_4)\\ 4H &\rightarrow 2H_2 \quad +2D(H_2)\\ C_{gas} &\rightarrow C_{diamond}+L(C)\\ \hline C_{gas}+4H &\rightarrow CH_4 \quad +D(CH_4) \end{aligned}$$

This shows that $D(CH_4)=Q(CH_4)+2D(H_2)+L(C)$, which yields

$$D(CH_4)=\left\{\begin{matrix}224.5 \pm 1.9 \text{ kcal.}\\ 9.84\pm0.08 \text{ volts}\end{matrix}\right\}+L(C) \quad (1)$$

on substitution of the above value of $D(H_2)$ and the value $Q(CH_4)=18.66$ kcal. or 0.81 volts.[16]

There is considerable uncertainty concerning the true value of $L(C)$. Bichowsky and Rossini[17] after reviewing all data published prior to Jan. 1, 1934 set the value at $170-a$ kcal., "where a is an unknown whose value at the present writing may be as much as +60 kcal." Recently data on predissociation in CO have set three possible values: $L(C)=168.8\pm0.5$ kcal., 123.6 ± 0.5 kcal., or 107.2 ± 0.5 kcal. These data cannot, however, decide which is the correct value since they do not reveal in what electronic states the C and O atoms are formed in a predissociation process. Goldfinger and Jeunehomme,[18] using these values to calculate vapor pressure *vs.* temperature curves for carbon, conclude that experimental curves, inaccurate as they may be, quite definitely rule out the lowest value and seem to favor the highest. However, their final conclusion is that the balance of evidence is in favor of the value

$$L(C)=123.6\pm0.5 \text{ kcal. or } 5.36\pm0.02 \text{ volts.} \quad (2)$$

Adopting this value one obtains from Eq. (1)

$$D(CH_4)=348.1\pm2.0 \text{ kcal. or } 15.10\pm0.10 \text{ volts.} \quad (3)$$

The location of level b in Fig. 5 at 4.5 volts above a is in agreement with the estimate of Norrish[19] from thermal and spectroscopic data. It also agrees with the results of Trenner, Morikawa, and Taylor[20] which show that the energy required for the reaction $CH_4\rightarrow CH_3+H$ at constant pressure and room temperature is almost certainly greater by a small amount than the heat of dissociation of hydrogen measured under the same conditions. Correcting the latter quantity[17] for the thermal energies of the reactants CH_4 and CH_3+H, one concludes that the level b must be slightly more than 102.4 kcal. or 4.44 volts above zero. Further evidence on this point is afforded by Voge's[21] theoretical calculations of the energies of formation, measured from the minima of the potential surfaces, of CH_4, CH_3, CH_2, and CH from normal carbon and hydrogen atoms. From the normal frequencies[22] of these molecules the author has calculated their zero-point energies to be: 1.17 volts, 0.82 volts, 0.46 volts, and 0.18 volts, respectively. If now for the energy of formation of CH_4 the value 16.27 volts (quantity (3)+1.17 volts) is used in Voge's equations, a new value for the energy of formation of CH_3 may be obtained which, when corrected by the zero-point energy of CH_3 and subtracted from (3), gives 4.40 volts or 101.4 kcal. as the height at which level b should be set above zero.

Level d must be below level e by $D(CH)$ for which the value 3.5 volts[4] has been adopted. Level c was located by adding the zero-point energy of CH_2 to Voge's result for the energy of formation of CH_2 based on the above value of $D(CH)$ and subtracting the result from $D(CH_4)$ (3).

(a) Positive ions

H^+.—The dissociation energy plus the total kinetic and excitational energy involved in the higher of the two appearance potentials of H^+ ions is $29.4-13.5=15.9\pm0.6$ volts, where 13.5 volts $=I(H)$. The dissociation process therefore

[15] Richardson and Davidson, Proc. Roy. Soc. **A125**, 23 (1929).

[16] This quantity was obtained from the value, reference 18, for the corresponding reaction under constant pressure at 18°C by correcting for the thermal energies of the reactants.

[17] Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, N. Y., 1936).

[18] P. Goldfinger and W. Jeunehomme, Proc. Faraday Soc. **32**, 1591 (1936). In this paper will be found an excellent bibliography of recent papers on this subject.

[19] R. G. W. Norrish, Trans. Faraday Soc. **30**, 106 (1934).

[20] N. R. Trenner, K. Morikawa and H. S. Taylor (paper soon to appear).

[21] H. H. Voge, J. Chem. Phys. **4**, 581 (1936).

[22] Frequencies of CH_4 and CH as well as those of the methyl halides from which those of CH_3 were estimated are given by Sponer, reference 4. The frequencies of CH_2 are given by Sutherland and Dennison (Proc. Roy. Soc. **A148**, 250 (1935)).

could be that represented by a transition from level a (Fig. 5) to any one of the higher levels except c' and e''. If this higher level is e the total excitational and kinetic energy which an H^+ ion, three H atoms, and a C atom must have when formed is $15.9-15.1=0.8\pm0.6$ volts; if it is any level lower than e at least 4.3 volts must be assigned to kinetic and excitational energy of the products of dissociation. It seems reasonable, therefore, to assume that the reaction wherein H^+ ions are formed at a minimum energy of 29.4 volts is: $CH_4\rightarrow H^+ + C + 3H$. Subject to the validity of this assumption, the following upper limits may be set:

$$\left.\begin{array}{l} D(CH_4)\leq 15.9\pm0.6 \text{ volts or } 366\pm14 \text{ kcal.} \\ L(C) \leq 6.1\pm0.6 \text{ volts or } 141\pm14 \text{ kcal.} \end{array}\right\} \quad (4)$$

This conclusion, if correct, cannot be reconciled with the value 168.8 ± 0.5 kcal.[18] for $L(C)$.

Subtracting $I(H)=13.5$ volts from 22.7 volts, one sees from Fig. 5 that the dissociation process involved in the formation of H^+ ions at 22.7 volts minimum energy must be one of the three represented by transitions from a to c, d', or b. The total kinetic and excitational energy of the products in these cases would be: $9.2-8.1=1.1$ volts; $9.2-7.1=2.1$ volts; or $9.2-4.5=4.7$ volts. Since the latter value seems high it is probable that these ions are produced either in the reaction $CH_4\rightarrow H^+ + CH_2 + H$ or the reaction $CH_4\rightarrow H^+ + CH + H_2$.

H_2^+.—It is evident from Fig. 5 that the dissociation energy involved in $A(H_2^+)$ is that required for one of the reactions whereby a CH_4 molecule is transformed to one of the four states e', d', e'', or c'. Since the dissociation plus kinetic and excitational energy is $27.9-15.4=12.5\pm0.5$ volts (where 15.4 volts $=I(H_2)$) it seems likely that the dissociation is to level e' rather than to a lower level, and hence that H_2^+ ions are formed in accordance with the reaction $CH_4\rightarrow H_2^+ + C + 2H$. The products must possess at least $12.5-10.6=1.9\pm0.5$ volts of kinetic energy or energy of excitation.

H_3^+.—If we let $D(H_3^+)$ stand for the unknown energy absorbed in the reaction $H_3^+\rightarrow H_2+H^+$ we have as the energy of the dissociation of CH_4 to a state involving three H atoms plus the total kinetic and excitational energy involved in $A(H_3^+)$: $A(H_3^+) + D(H_3^+) + D(H_2) - I(H) = 16.3\pm1.0$ volts $+D(H_3^+)$. In accordance with previous reasoning this state must be either d or e of Fig. 5. This would indicate that H_3^+ ions are probably formed in the reaction $CH_4\rightarrow H_3^+ + C + H$, the energy required to excite or give kinetic energy to the products being $\{16.3+D(H_3^+)\}-15.1=1.2\pm1.0$ volts $+D(H_3^+)$. However, it appears that in the case of these ions one should consider the possibility that products of dissociation formed along with a positive ion may be negatively charged as well as neutral. A consideration of the negative ions (see below) shows that possibly an H_3^+ ion is formed together with a CH^- ion (but that negative ions need not be considered in the interpretations of the observed appearance potentials of any other type of positive ion).

C^+.—There are three transitions $a\rightarrow e''$, $a\rightarrow e'$, and $a\rightarrow e$ (Fig. 5), the energy required for which could be the dissociation energy involved in $A(C^+)$. Subtraction of $I(C)=11.2$ volts from 26.7 ± 0.7 volts yields 15.5 ± 0.7 volts as the sum of this dissociation energy and any kinetic or excitational energy with which the products may be formed. It therefore seems most reasonable to assume that C^+ ions are formed according to the reaction $CH_4\rightarrow C^+ + 4H$, the total kinetic and excitational energy of $C^+ + 4H$ being $15.5-15.1=0.4\pm0.7$ volts. If this assumption is correct the observation $A(C^+)=26.7\pm0.7$ volts leads to the conclusion:

$$\left.\begin{array}{l} D(CH_4)\leq 15.5\pm0.7 \text{ volts or } 357\pm16 \text{ kcal.,} \\ L(C) \leq 5.7\pm0.7 \text{ volts or } 131\pm16 \text{ kcal.} \end{array}\right\} \quad (5)$$

Here again we have fairly strong evidence against the value $L(C)=168.8\pm0.5$ kcal.[18]

CH^+.—There are two possible reactions which could account for the production of CH^+ ions from CH_4 molecules: (a) $CH_4\rightarrow CH^+ + 3H$; and (b) $CH_4\rightarrow CH^+ + H + H_2$. If (a) is correct $I(CH) \leq A(CH^+) - \{D(CH_4) - D(CH)\} = 11.7\pm0.6$ volts (according as the products of dissociation are formed with or without excitational and kinetic energy), while if (b) is correct $I(CH)\leq 11.7 + D(H_2) = 16.2\pm0.6$ volts. No data on $I(CH)$ which might enable one to choose between (a) and (b) exist.[23]

[23] In a previous paper, reference 1, the value 150 kcal. was calculated for $L(C)$ from the difference between $A(CH^+)$ and the appearance potential of CH^+ ions formed in acetylene. The reasonableness of this value was

CH_2^+.—Since there are two appearance potentials for CH_2^+ ions and only two reactions whereby they may be formed it seems quite probable that 15.7 ± 0.5 volts is the minimum energy required for the process $CH_4\rightarrow CH_2^+ + H_2$ while 22.9 ± 0.8 volts is that required for the process $CH_4\rightarrow CH_2^+ + 2H$. Thus, from the energies required for the corresponding dissociations without ionization (Fig. 5), we may conclude that $I(CH_2)\leq 15.7-3.7=12.0\pm0.5$ volts, and hence that the products of the reaction requiring 22.9 volts must dissociate with at least $22.9-(8.1+12.0)=2.8$ volts of kinetic and excitational energy.[24]

CH_3^+.—Simple considerations show that 14.4 ± 0.4 volts is the minimum energy required to produce CH_3^+ ions according to the reaction $CH_4\rightarrow CH_3^+ + H$. This means that $I(CH_3)\leq 14.4-4.5=9.9$ volts according as the CH_3^+ ions and H atoms are formed with or without energy. This is not in very good agreement with either Fraser and Jewett's value of 11.1 ± 0.5 volts[25] obtained by direct measurement on free CH_3 radicals or with Mulliken's theoretical estimate of 8.5 volts.[26]

(b) Negative ions

The curves shown in Fig. 4 are characteristic of ion current *vs.* electron energy curves for negative ions formed in various substances. The interpretation which is at present accepted of such curves[27] is that a peak at low electron energies indicates the formation of a negative ion through dissociation of a molecule and capture of the impacting electron, while the rising of a curve to a broad maximum at higher energies corresponds to the dissociation of molecules into pairs of positive and negative ions. No explanation of the apparent upward breaks at ~47 volts, 50 volts, and 45 volts in the curves of Fig. 4 for H^-, C^-, and CH^-, respectively, has been attempted. It is quite possible that these are due to some peculiarity of the apparatus and not to the formations of negative ions according to reactions different from those requiring lower energies.

H^-.—Taking $E(H)=0.7$ volt,[28] we see from Fig. 5 that the following are the four possible processes requiring least energy according to which H^- might be formed by dissociation and capture:

(a) $CH_4\rightarrow CH_3+H^-$ -3.8 volts;

(b) $CH_4\rightarrow CH+H_2+H^-$ -6.4 volts;

(c) $CH_4\rightarrow CH_2+H+H^-$ -7.4 volts;

(d) $CH_4\rightarrow C+H+H_2+H^-$ -9.9 volts.

The observation that H^- ions are formed in three different processes all requiring less energy than (d) suggests rather strongly that (a), (b) and (c), respectively are the reactions occurring at the observed minimum energies 6.1 ± 0.3 volts, 6.9 ± 0.8 volts, and 7.3 ± 1.0 volts. This interpretation requires that the total kinetic and excitational energies of the products formed be at least $6.1-3.8=2.3$ volts in reaction (a), $6.9-6.4=0.5$ volt in reaction (b), and $7.3-7.4\leqq 0$ volts in reaction (c).

If we take $I(CH)=11.7$ volts and $I(CH_2)=12.0$ volts Fig. 5 indicates that the 18.0-volt appearance potential of H^- can only be the minimum energy for one of the reactions $CH_4\rightarrow H^-+CH_3^+$ or $CH_4\rightarrow H^-+CH^+ + H_2$. The energy required for the first of these would be 14.4 volts (that needed for the reaction $CH_4\rightarrow H+CH_3^+$) $-E(H)$ or 13.7 volts plus the kinetic and excitational energy of $H^-+CH_3^+$. Hence the latter energy would be 4.3 volts. The energy required for the second reaction, aside from the kinetic and excitational energy of $H^-+CH^+ + H_2$, would be 7.1 volts $+I(CH)-E(H)$ or 18.1 volts. Thus if H^- ions are produced according to this process the products can be formed in their normal states with practically no mutual kinetic energy. Because of the relatively strong CH_3^+ ionization and unresolved ion current at $m/e=13$ produced at minimum energies less than 18.0 volts, neither the CH_3^+ ions, if formed in the first reaction, nor the CH^+ ions, if formed in the second reaction, at 18.0 volts minimum energy could have been detected.

taken to be evidence in favor of reaction (*a*). However, on the assumption that reaction (*b*) is correct and that CH^+ ions are produced from C_2H_2 molecules in the process $C_2H_2\rightarrow CH^+ + CH$ one obtains by a similar calculation $L(C)=128$ kcal.

[24] The conclusions with regard to CH_2^+ ions in a previous paper, reference 1, were less definite because of doubt as to the reality of the appearance potential at 22.9 volts. This doubt has since been largely dispelled.

[25] R. G. J. Fraser and T. N. Jewett, Phys. Rev. **50**, 1091 (1936).

[26] R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933).

[27] W. W. Lozier, Phys. Rev. **46**, 268 (1934).

[28] Hylleraas, Zeits. f. Physik **65**, 208 (1930).

C^-.—The striking feature of the curve shown in Fig. 4 for C^- ions is the absence of a detectable peak at low electron energies. From this it appears that a C^- ion is only formed along with a positive ion. This ion may be H^+, H_2^+, or H_3^+. The assumption that the reaction $CH_4 \rightarrow C^- + H + H_3^+$ occurs at a minimum energy of 27.4 ± 0.6 volts seems distinctly unreasonable on the grounds that the additional H_3^+ ionization would have been detected in the appearance potential curve for that ion. It is quite possible that 27.4 ± 0.6 volts may be identified with the 27.9 ± 0.5 volt appearance potential of H_2^+ ions. The fact that at an electron energy of 50 volts H_2^+ ionization is about 80 times as intense as C^- ionization shows that most of the H_2^+ ions are formed according to some reaction (a) other than (b) $CH_4 \rightarrow C^- + 2H + H_2^+$. From the discussion of $A(H_2^+)$ it is evident that probably (a) is the reaction $CH_4 \rightarrow C + 2H + H_2^+$. The minimum energy required for (b) should, except for differences in the kinetic and excitational energies of the products, be less than that required for (a) by $E(C) = 1.9 \pm 0.7$ volts.[29] However, in the appearance potential curve for H_2^+ there is no abrupt change of curvature at electron energies above 27.9 volts showing that if both (a) and (b) take place the minimum energies required are about the same and hence that $C^- + 2H + H_2^+$ must possess about 1.9 volts more energy when formed than $C + 2H + H_2^+$.

A simpler and more likely explanation of the formation of C^- ions is provided by the assumption that they are accompanied by H^+ ions. The intensity of H^+ ionization is $\sim 10^3$ times that of C^- ionization at 50 volts electron energy. Hence we should not expect to detect the appearance of the relatively small H^+ ionization produced in the process $CH_4 \rightarrow C^- + 2H + H^+$ at 27.4 volts minimum energy. Without allowance for excitational and mutual kinetic energies of the products the minimum energy for this process should be $D(CH_4) + I(H) - E(C) = 26.7 \pm 0.7$ volts. Hence on this assumption we may conclude that the products possess at least $27.4 - 26.7 = 0.7 \pm 0.9$ volts of energy, or that $D(CH_4) \leq A(C^-) + E(C) - I(H)$ and hence that[29]

$$\left.\begin{aligned} D(CH_4) &\leq 15.8 \pm 0.9 \text{ volts or } 364 \pm 21 \text{ kcal.,} \\ L(C) &\leq 6.0 \pm 0.9 \quad \text{“} \quad \text{or } 139 \pm 21 \quad \text{“} \quad . \end{aligned}\right\} \quad (6)$$

The latter conclusions like (4) and (5) provides fairly strong evidence against the value 168.8 kcal.[18] for $L(C)$.

CH^-.—The first appearance potential of CH^- ions may readily be explained as the energy required for the process $CH_4 \rightarrow CH^- + 3H$. This yields the result that $E(CH) \geq 11.6 - 10.2 = 1.4$ volts according as the products are formed with or without energy. The other reaction ($CH_4 \rightarrow CH^- + H + H_2$) which could account for these ions demands that the products be formed with an energy of 2.1 volts $+ E(CH)$. The second appearance potential of CH^- ions could be the minimum energy for the reaction $CH_4 \rightarrow CH^- + H_3^+$. This interpretation is indicated by the agreement of $A(CH^-) = 24.5 \pm 0.5$ volts with $A(H_3^+) = 25.3 \pm 1.0$ and by the fact that the intensities of H_3^+ and CH^- ionizations are approximately equal at all electron energies at least as high as 60 volts. Again using $D(H_3^+)$ to represent the energy of the reaction $H_3^+ \rightarrow H_2 + H^+$, we see from Fig. 5 that only 20.6 volts $- E(CH) - D(H_3^+)$ should be required to break a CH_4 molecule apart into a CH^- ion and an H_3^+ ion in their normal states without mutual kinetic energy. Hence if this be the correct interpretation the amount of the impacting electron's energy which must go into kinetic and excitational energy of the two ions is 3.9 volts $+ E(CH) + D(H_3^+)$.

The process whereby a CH^- ion and other products of a CH_4 molecule could be formed with the least total kinetic and excitational energy is $CH_4 \rightarrow CH^- + 2H + H^+$. Here we see from Fig. 5 that this energy would be $(24.5 - 25.1)$ volts $+ E(CH)$ and is $\geq 0.8 \pm 0.6$ volts if we take $E(CH) \geq 1.4$ volts as indicated in the previous paragraph.

CH_2^-.—When a CH_2^- ion is produced by dissociation of a CH_4 molecule and capture of the impacting electron, the other atoms of the original molecule may dissociate as 2H or as H_2. The energy required to excite or give kinetic

[29] The author estimated the value $E(C) = 1.9 \pm 0.7$ volts by plotting the square roots of the ionization potentials of N, O^+, and F^{++} *vs.* their atomic numbers and extrapolating to atomic number six. Glockler (Phys. Rev. **45**, 111 (1934)), by a similar extrapolation, has obtained the value 1.37 volts for $E(C)$. Use of this value instead of 1.9 volts lowers the total excitational and kinetic energy of products as well as the upper limits (6) for $D(CH_4)$ and $L(C)$ by 0.5 volts or 12 kcal.

TABLE IV. *Values calculated for $D(CH_4)$ and $L(C)$.*[29]

BASIS OF CALCULATION	$D(CH_4)\leq$	$L(C)\leq$
$A(H^+)=29.4\pm0.6$ volts	15.9 ± 0.6 volts or 366 ± 14 kcal.	6.1 ± 0.6 volts or 141 ± 14 kcal.
$A(C^+)=26.7\pm0.7$ volts	15.5 ± 0.7 volts or 357 ± 16 kcal.	5.7 ± 0.7 volts or 131 ± 16 kcal.
$A(C^-)=27.4\pm0.6$ volts	15.8 ± 0.9 volts or 364 ± 21 kcal.	6.0 ± 0.9 volts or 139 ± 21 kcal.

energy to the products formed would be 0.8 volts$+E(CH_2)$ in the first case or 5.2 volts $+E(CH_2)$ in the second case. Since the latter value seems high it is probable that the reaction occurring is $CH_4\rightarrow CH_2^-+2H$. The formation of a CH_2^- ion at energies greater than 23.4 ± 0.6 volts must proceed according to one of the two reactions $CH_4\rightarrow CH_2^-+H+H^+$ or $CH_4\rightarrow CH_2^-+H_2^+$. Aside from the excitational and mutual kinetic energies of the products, the minimum energies for these two reactions are respectively: 21.6 volts$-E(CH_2)$; and 19.0 volts$-E(CH_2)$. Thus the total kinetic and excitational energies of the products must be: 1.8 volts$+E(CH_2)$; or 4.4 volts$+E(CH_2)$. It is unlikely that the positive ions formed in one or the other of these processes would be sufficiently numerous to be distinguishable from those formed in other ways.

SUMMARY AND CONCLUSION

A summary of the conclusions which were drawn in the above discussions from the values of dissociation energies given in Fig. 5 will be found in the last three columns of Table I. The values in column five are calculated by adding ionization energies to these dissociation energies. They represent minimum energies for the corresponding reactions exclusive of the total kinetic or excitational energy products must have when formed by electron impact. Values of the latter quantities are given in column six where possible and are obtained by subtraction of the values of column five from the corresponding appearance potentials in column three.

It should be emphasized that the quantities of Fig. 5 are not certain and that hence some of the interpretations may be incorrect. One cannot be completely sure at present of any reaction except (12) and (13). However, it is a fact of considerable significance that a reasonable explanation for every observed appearance potential exists. Attention should be drawn specifically to the fact that in all cases except $A(CH_2^+)=22.9$ volts, $A(H^-)=6.1$ volts, and probably the appearance potentials of H_3^+ and CH_2^-, interpretations are possible which require that the total excitational and kinetic energy of products formed by electron impact from CH_4 molecules be less than two volts.

It will be noted that the ions H_2^+, H_3^+, C^+, C^-, CH^-, and CH_2^- are not produced unless in each case the energy of the electrons is at least slightly greater than the largest of the calculated minimum energies for possible processes. This may be true of CH^+ ions as well. The higher of the two appearance potentials of H^+ and the higher appearance potential of CH_2^+ also satisfy this condition. The only type of ion for which an appearance potential satisfying this condition was not detected is H^-. These facts seem to indicate that at least in most of the cases mentioned, the possible processes which require the largest calculated minimum energies are the ones which actually take place: i.e., that most ions are only formed when the parent molecules are broken into as many parts as possible. This conclusion gives one some reason to prefer the reactions (5), (8), (21), and (24) to the reactions (6), (9), (22), and (25) (column four of Table I).

This conclusion also adds weight to the relations (4), (5), and (6) which are gathered together in Table IV. These relations are based on the assumptions that the appearance potentials in column one of Table IV are minimum energies for the reactions (3), (7), and (19) in column four of Table I. The values quoted are in each case less than or equal to the true values of $D(CH_4)$ and $L(C)$ according as the total excitational and kinetic energies of the products is greater than or equal to zero. Thus as a further conclusion, we may say that of the three values of $L(C)$ determined from a predissociation limit in CO[18], the results for methane provide good evidence against the value 168.8 kcal. and are completely consistent with the value 123.6 kcal. They are also consistent with the lower of the two possible

values (136 kcal.) obtained by Lozier[27] from data on the products formed by electron impact in CO.

In closing the author wishes to thank Professor Walker Bleakney, under whose direction this work was done, and Professors E. U. Condon and H. D. Smyth for many helpful suggestions. He also would like to express appreciation to Drs. W. Wallace Lozier and Philip T. Smith who, with Professor Bleakney, designed and constructed the apparatus with which this work was done and to Mr. Kiyoshi Morikawa of the chemistry department of Princeton University for supplying samples of very pure methane.

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Thermionic Emission into Dielectric Liquids

EDWARD B. BAKER AND HOWARD A. BOLTZ
The Detroit Edison Company, Detroit, Michigan

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The presence of thermionic emission at ordinary temperatures for cathodes in contact with dielectric liquids is demonstrated. The current voltage relation is shown to obey the law $I=I_0e^{(\epsilon(\epsilon FD)^{\frac{1}{2}}/kT)}$, where I is the current, F the field, and D the dielectric constant of the liquid. This is a modification of the Schottky law in vacuum. The effects of adsorbed hydrogen and oxygen, of surface irregularities, and of work function are discussed. The formation of a wax by electron bombardment of the liquid is also reported.

A. INTRODUCTION

MANY theories have been advanced to explain the mechanism of current conduction in pure dielectric liquids in the region of high field strengths. A good resume of these may be found in Nikuradse's book.[1] The most generally accepted of these is the process of ionization by collision, in analogy to gaseous conduction. It is assumed that ions are initially present in the liquid which are the current carriers at low field strengths. These are supposed to be formed by some ionizing agent such as x-rays or cosmic rays, or from ordinary electrolytic dissociation. At intermediate field strengths this ion current saturates and becomes independent of field until such a value is reached that the ions (or electrons) attain sufficient velocity to form new ions by collision. New ions are formed at such a rate that the current becomes an exponential function of the voltage $I=I_0e^{cV}$ which is found to agree fairly well with experiment, considering I_0 and C as adjustable constants. Most published data available to the authors are not sufficiently accurate, however, to distinguish this relation from $I=I_0e^{c\sqrt{V}}$, for example.

In contrast to the above view, the results obtained in our investigation prove that, in the case of the liquid investigated (pure toluene), at least, the only important means of current conduction is by electrons emitted from the cathode thermionically.

This mechanism was first proposed in tangible form by H. Edler and O. Zeier[2] who found the temperature variation of the current to correspond to the Richardson equation for thermionic emission. Although they did not derive the current voltage relation given in this paper they found the current to vary less rapidly with voltage than $I=I_0e^{cV}$.

L. Inge and A. Walther[3] also disagree with the mechanism of ionization by collision and invoke instead the cold cathode effect, which would require a current voltage relation of the form $I=I_0V^2e^{-c/V}$. They plot essentially $\log I/V^2$ against $1/V$ and obtain not a straight line, but a curve which they believe to be approaching a straight line in its high voltage portion. However, if their data are replotted as $\log I$ against $\sqrt{V}$, a straight line is obtained in verification of the formula $I=I_0e^{c\sqrt{V}}$ of the present paper.

[1] A. Nikuradse, *Das flüssige Dielektrikum*, pp. 135–136.

[2] H. Edler and O. Zeier, Zeits. f. Physik **84**, 356 (1933).

[3] L. Inge and A. Walther, Tech. Phys. U. S. S. R. **1**, 539 (1935).

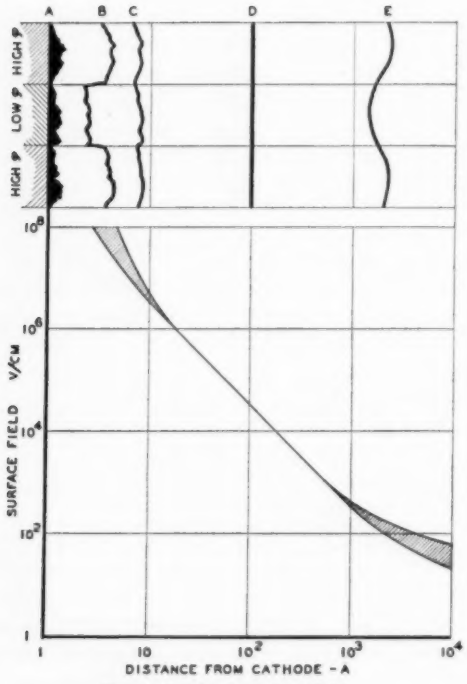

FIG. 1. Intrinsic surface fields.

B. THEORY

I. In vacuum

The emission of electrons from a hot cathode in a vacuum is governed by the well-known Richardson law, $I=AT^2e^{-\epsilon\varphi/kT}$ where I is the current density, φ is the work function in electron volts and $\epsilon\varphi=\chi$ is the amount of energy required to remove an electron from the metal to a vacuum. If a sufficient extracting field is applied to the cathode the current becomes saturated except for the Schottky correction, which introduces a dependence upon the field F of the form

$$I=AT^2e^{-\epsilon\varphi/kT}e^{\epsilon(\epsilon F)^{\frac{1}{2}}/kT}=I_0e^{\epsilon(\epsilon F)^{\frac{1}{2}}/kT}.$$

This Schottky relation, suitably altered to include the effect of a medium possessing a dielectric constant greater than unity, provides the limiting form at high fields of the current-voltage relation for electronic conduction in a dielectric liquid. Before introducing this modification, it will be convenient to make a few remarks about the Schottky law in vacuum which will also be pertinent when the dielectric liquid is present.

Becker and Mueller[4] have shown that the electrons emitted from the cathode surface must have a normal component of velocity sufficient to project them beyond the attracting influence of the surface fields, into the region where these fields are smaller than the external extracting field. They have shown that these fields may be divided into three classes according to their range of action. First, are the powerful but extremely short range fields of the metal atoms that are responsible for the major portion of the work function. Second, are the image forces which predominate out to about 10^{-5} cm. At still greater distances, forces due to nonuniformities of the work function over the surface are most important.

At the actual surface of the metal the atomic fields are of the order of 10^8 volts/cm which is the magnitude required for the cold cathode effect. Moving out from the cathode, the intrinsic field falls off rapidly and it is possible to neutralize it, or to produce a surface of zero field strength, by applying an external field. The distance of this surface of zero field from the cathode is dependent upon the strength of the applied field. On the cathode side of this surface, the net field is in the sense that tends to return electrons to the cathode, and on the other to send them to the anode. An electron consequently must have sufficient initial velocity to reach this surface against the adverse field in order to be emitted.

In Fig. 1, the surface fields are plotted against distance on a logarithmic scale. In the range in which the image field predominates, the curve becomes a straight line corresponding to the function $F_i=\epsilon/4z^2$, where z is the distance of the electron from the cathode, and ϵ is its charge. Above several hundred angstroms the patch fields are most important and below about 10A the atomic fields of the metal atoms assume control. Each end of the curve is shown to broaden out, representing the possible variations in value of the field at various points over a plane surface parallel to the plane cathode, due to patchy work function, and in the case of the short range fields, to surface irregularities as well.

A cross section showing the zero field surfaces

[4] J. A. Becker and D. W. Mueller, Phys. Rev. **31**, 431 (1928).

for various applied fields is pictured above the graph. If the metal surface, A, is not perfectly plane and of uniform work function, only those zero field surfaces, such as D lying within the effective range of the image force will be plane.

The geometrical surface irregularities that exist even on a highly polished electrode cause deviations from the Schottky law at high applied fields. Points cause most of the emission from a surface of uniform work function, if the applied field is high enough to cause the surface of zero field (C) to be appreciably distorted by their presence. Thus, the more nearly flat the cathode is, the higher must be the applied field, or the closer to it must be the surface of zero field, in order to have the effect of points of any consequence. In investigating the cold cathode effect, it must be flat even on an atomic scale in order to avoid the influence of points.

If the applied field is F, and the surface is perfectly plane, we have the ordinary Schottky relation. If, however, a point exists on the surface, the applied field at the tip of the point is not F but p_0F, where p_0 is a field factor (>1) depending on the sharpness of the point. At the surface of zero net field, the applied field is pF, where p is a function of F, equal to p_0 at the point and becoming unity at a sufficient distance from the cathode. The Schottky relation for the current from the point is

$$I = I_0 e^{\epsilon(\epsilon pF)^{\frac{1}{2}}/kT}.$$

If the point is sufficiently sharp, i.e., if p is large, the contribution of current from the point may overshadow that for all the remainder of the surface. This modified relation may be approximately obeyed if a number of points of about the same size exist simultaneously.

Since p is a function of F, a straight line will not be obtained if log I is plotted against $\sqrt{F}$ as is commonly done to illustrate the Schottky effect. Instead, a curved line having increasingly greater slope with increasing field will result. However, if p is a slowly varying function of F, the curvature is slight and the curve may appear straight over the portion investigated, but will be too steep. Since the knee of the curve log I *vs.* $\sqrt{F}$ obtained experimentally (caused by the approach to the limiting Schottky line) has the opposite curvature, a point of inflection is produced and the appearance of straightness enhanced.

The Schottky law is derived on the assumption that the image law force $F_i = \epsilon/4z^2$ is the only long range force of importance. This is accomplished[5] by showing that an external field, F, produces a change $\Delta\varphi = (\epsilon F)^{\frac{1}{2}}$ in the effective work function by neutralization of the image force at the critical distance $z_c = (\epsilon/4F)^{\frac{1}{2}}$ from the cathode surface. At lower applied fields the effect of the patch fields overshadows the image law and the Schottky law does not apply.

II. Modification introduced by the presence of a dielectric liquid

If we replace the vacuum by a dielectric liquid we may expect the phenomenon to be altered by the following considerations:

1. *The work function will be lowered* because the amount of energy necessary to transfer an electron from the metal to a vacuum is greater than that required to transfer it to a dielectric liquid. This difference in energy corresponds to the energy necessary to remove a "free" electron from the liquid to a vacuum. By a free electron in a dielectric liquid we mean an electron not in "chemical" combination with molecules of the liquid but simply immersed in it, the polarizing forces its field exerts on the surrounding molecules of the liquid being responsible for the difference of energy in question, which we may term the "heat of immersion of an electron." We may expect that this amount of energy will be independent of the nature of the metal, and as a result that the relative order of the metals in the photoelectric series will be the same as in vacuum. We may also predict that the amount of the lowering of the work function will be at least roughly dependent upon the dielectric constant of the liquid, being greatest for liquids of highest dielectric constant.

2. *The temperature used must be lower* since the dielectric liquid would boil or decompose at the temperatures used in studies of thermionic emission in vacuum. Since T and φ occur in reciprocal relation in the exponent of Richardson's formula, we may expect that a lowering of both T and φ simultaneously will permit appreciable emission

[5] J. Becker, Rev. Mod. Phys. **7**, 108 (1935).

at room temperature, if φ is lowered to such an extent that the ratio is not greatly altered.

3. *The saturation of the current will be much less complete* at high fields partly because the temperature is lower; the exponent in the Schottky correction is consequently larger, and the dependence on the field of more importance. In addition, the Schottky correction must be modified by the fact that the image force is weakened by the presence of a liquid of dielectric constant greater than one. The image force in a dielectric of dielectric constant D is $F_i=\epsilon/4z^2D$, the distance from the cathode of the surface of zero field is $z_c=(\epsilon/4FD)^{\frac{1}{2}}$, and the revised Schottky correction is

$$I=I_0e^{\epsilon(\epsilon FD)^{\frac{1}{2}}/kT} \quad \text{or} \quad \log_{10}\frac{I}{I_0}=\frac{1.91(FD)^{\frac{1}{2}}}{T}$$

with F in volts per cm.[6] This is the form that the current voltage characteristic takes at high fields. The slope of the line $\log_{10} I=c\sqrt{F}+\log I_0$ is much greater than in a vacuum.

As a rule, somewhat higher fields are required to obtain the straight line portion of the curve than is the case in vacuum. For a given field strength, the surface of zero field as determined by $Z_c=(\epsilon/4FD)^{\frac{1}{2}}$ lies closer to the cathode, and the effect of points on the surface is much more pronounced. Stated in other words, in order to avoid the effect of points, a much smoother surface must be employed as cathode in a dielectric liquid, than is necessary in vacuum.

4. *Collisions of electrons with, and attachment to molecules of the liquid may interfere* with the direct application of the theory of emission in vacuum to that in a liquid. Evidently, however, these are of minor importance for toluene since the data agree with the modified Schottky equation. At low fields collisions and attachment to molecules may be of importance but it would be difficult to distinguish their effects from effects caused by patchy fields.

The authors have observed evidences of chemical action caused by electron bombardment. If high field strengths are used and electrode conditions are such that high currents are flowing, enough of a wax-like substance is deposited on the anode to be readily discernible in about a week's time. This substance is similar in appearance, and in its complete insolubility in organic liquids, to the substance called X which is often observed in underground power cables having oil and paper as a dielectric. Its presence there has always been ascribed to electron bombardment, resulting from discharges in gas pockets in the insulation. This work, however, shows that it may also be produced in the liquid phase alone by electrons produced thermionically, and therefore that its presence does not presuppose the existence of gas pockets, or voids.

It is conceivable that the molecules of some liquids might have sufficient electron affinity seriously to impair or completely to suppress the electron emission altogether by attaching the electrons before they reach the surface of zero field. In such an event the ions thus formed would be discharged again at the cathode.

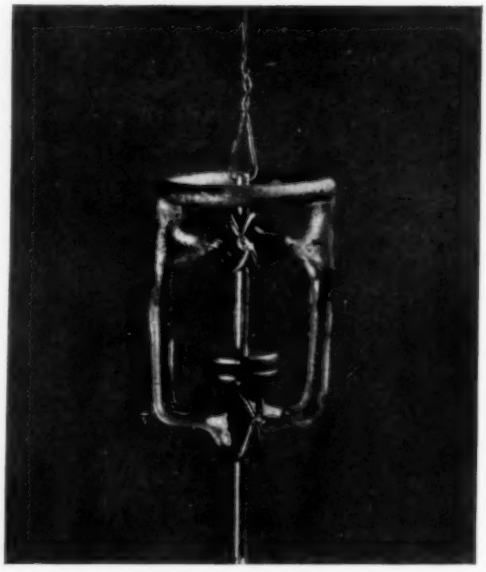

FIG. 2. The electrodes and quartz support.

C. APPARATUS

The electrodes used were platinum-iridium and nickel, turned to the form shown in Fig. 2. The faces were ground flat and polished on a metallographic wheel. The electrodes were then tied with wire of the same metal to the small quartz

[6] One may obtain this expression by introducing the new value of the image force in Becker's derivation of the Schottky correction (reference 5).

frame shown, being aligned by means of grooves ground in the quartz. The bottom electrode shank was drilled so that the assembly could rest on a tungsten point serving as a high voltage lead in. The upper electrode was drilled perpendicular to its axis near the end to receive a stiff platinum wire serving as a measuring lead and as a means of carrying the assembly.

The quartz ring shown was platinized. It made contact with a platinized ring in the apparatus proper, and served as a leakage guard. A guard to preserve a uniform field is neither necessary nor desirable.

The electrode distance was determined by means of a traveling microscope after the assembly was in place.

The apparatus proper is shown in Fig. 3. It consists of a boiler containing toluene and metallic sodium, a central mixing chamber and the electrode chamber. It was designed to permit ready accessibility to the electrodes and the addition of soluble impurities to the toluene without allowing the entrance of air or moisture. By continued distillation from sodium the toluene is constantly repurified and desiccated, and the electrode chamber is continually washed out with fresh toluene.

Since the present work is concerned only with the demonstration of the presence of thermionic emission and the agreement with the modified Schottky law, the absolute value of the work function itself is of importance only insofar as it effects the general order of magnitude of the currents obtained. Consequently, it is not necessary to work in high vacuum, which would be extremely difficult in the presence of an organic liquid. A nitrogen atmosphere was maintained, however, partly to avoid oxidation of the toluene during distillation, and partly because adsorbed nitrogen is known[7] to have a comparatively small effect on the work function of a cathode in vacuum. The effect of other adsorbed gases will be treated in connection with the experimental results.

The toluene vapor leaving the boiler passed over metallic sodium held in a bend in the tube leading from the boiler to further aid in removing moisture, part of which may distill before it can react with the sodium immersed in the toluene. The vapor condensed in the two water condensers, which served to protect from the vapor the ground glass joints, by means of which the electrodes and foreign substances were introduced.

FIG. 3. The electrode chamber and still.

A stopcock attached to a cross arm connecting the two entrance tubes led to a P_2O_5 drying tube, a pyrogallol bulb and a rubber bag reservoir. A stream of nitrogen flowed through this train whenever a joint was opened, preventing the influx of air and moisture.

A siphon connected the mixing reservoir with the electrode chamber permitting either a continuous flow of toluene from one to the other or an accumulation of toluene in the mixing chamber, which may later be run through the electrode chamber. This is accomplished by tilting the apparatus, which introduces a few gas bubbles

[7] J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge Press, 1935), p. 147.

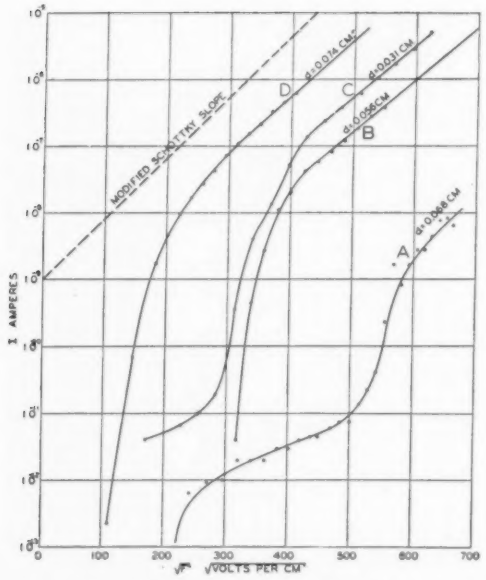

FIG. 4. Current-voltage characteristics for *A* oxygen on platinum-iridium, and *B*, *C*, *D* hydrogen on platinum-iridium. Temperature was 45°C.

in the siphon, stopping its action until the level in the mixing chamber is high enough to start the siphon again. Foreign materials may be added to the accumulated toluene, which is then siphoned to the electrode chamber.

In some cases the electrodes were heated in vacuum by means of radiofrequency induction, cooled and then quickly transferred to the apparatus, exposing them to the air only for a short time. In this way the nature and amount of adsorbed gases could be controlled sufficiently well for the present purpose.

The electrical equipment has been described previously.[8]

The toluene used was C.P. grade further treated with mercury, concentrated sulphuric acid, sodium hydroxide, washed with water, and distilled from metallic sodium before introduction into the apparatus.

D. Experimental Results

The electrodes first used were made of platinum-iridium, because they were easy to clean by washing with chromic acid, then with distilled water and finally heating in a gas flame. Extremely low conductivity was observed even at high field strengths the first few times they were treated in this manner. Thereafter the conductivity became progressively higher with each treatment although there was no reason to suspect any change in the composition of the toluene. It was suspected that the electrodes had absorbed hydrogen from the flame, and heating them in a vacuum confirmed this.

Evidently an adsorbed layer of hydrogen lowers the work function in the same manner as in vacuum.[9] Now it is well known that it is extremely difficult completely to outgas platinum by heating in vacuum, but that it is easily possible to replace an adsorbed layer of hydrogen by one of oxygen, by heating platinum in oxygen, and conversely oxygen may be displaced by heating in hydrogen. Nitrogen, however, has little tendency to be adsorbed, or if adsorbed, does not appreciably affect the work function of platinum.

These facts offer a method of control of the condition of the surface, even if the electrodes be transported through air after the desired condition is attained. It was found possible to produce low or high conductivity at will by having a layer of oxygen or of hydrogen on the surface. Fig. 4 shows current-voltage characteristics for platinum-iridium electrodes plotted as log I *vs.* $\sqrt{F}$. Curve *A* is for adsorbed oxygen and curves *B*, *C* and *D* for adsorbed hydrogen. Comparing curves *A* and *D*, we observe a ratio of the currents of the order of 10^5, an enormous difference, which incidentally proves that all but an entirely negligible portion of the current represented by curve *D* is due to electrode condition, since the purity of the toluene was the same for *A* and *D*. This eliminates the possibility of the current being due to ions generated in the liquid by ordinary electrolytic dissociation, even at fields as low as 10 kv/cm.

Adsorbed layers of hydrogen and oxygen on platinum are present,[10] at least for the most part, in ionic form. In the case of hydrogen the ions are positive. This positively charged layer lowers the effective work function by tending to attract electrons out of the metal surface. Together with

[8] E. B. Baker and H. A. Boltz, Rev. Sci. Inst. **7**, 50 (1936).

[9] Cf. de Boer, reference 7, pp. 149–151.

[10] de Boer, reference 7, p. 150.

their image charges in the metal these ions form dipoles which on the cathode are oriented in the same direction as the applied field. In addition they are to a certain extent mobile on the surface,[11] even at room temperature. On a perfectly flat cathode, i.e., where the applied field is strictly constant, there will be no tendency for these dipoles to be displaced by the field. If, however, hills and valleys exist, they will be driven to the valleys, toward the regions of lowest field. The oxygen dipoles, since their orientation cannot be greatly influenced by the applied field, will be driven to the points. When the applied field is removed, they will again distribute themselves more uniformly over the surface by virtue of their mutal repulsion and by thermal diffusion.

Since an adsorbed layer of hydrogen lowers the work function, and since the hydrogen ions are driven to the valleys on the cathode, where the applied field is *less* than that calculated from the applied voltage and the distance with the assumption that the cathode is plane, we may expect that the slope of the Schottky line will be *less* than for a plane surface, i.e., $p<1$. That this is indeed the case may be observed in curves *B*, *C* and *D* of Fig. 4.

In the case of adsorbed oxygen the ions are driven to the points, but since oxygen increases the work function, the points are thereby rendered relatively inactive and the remainder of the surface being partially cleared of oxygen by the field, contributes most of the current, by virtue of its lower work function. This fact enables us to obtain a closer agreement with the theoretical slope, since the remainder of the surface, devoid of the points, is practically flat. This could not be done in the case of platinum because the approach to the Schottky line lies at such high field strengths (curve *A*) that breakdown is too imminent. In fact, while the current from oxygen on platinum is very low, it is erratic due to the sporadic removal of oxygen by the applied field, which suddenly exposes points of relatively low work function. Thus while an adsorbed layer of oxygen serves as a protection from large electron currents, its removal by the field may perhaps be a cause of breakdown for

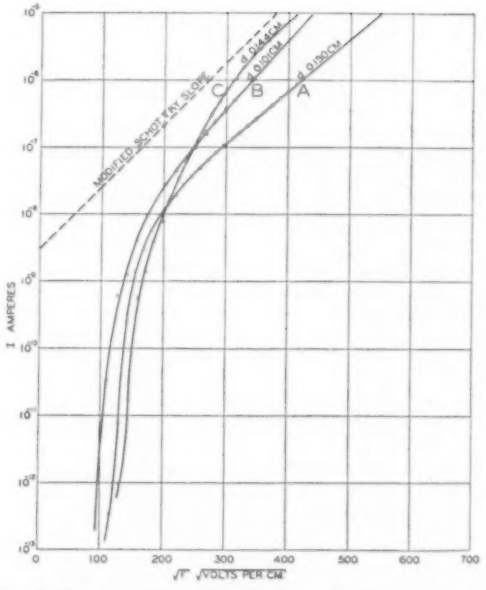

FIG. 5. Current-voltage characteristics for *A* and *C* hydrogen on nickel and *B* nickel. Temperature was 45°C.

electrodes in this condition, and electrodes usually *are* in this condition unless specially treated.

It may be emphasized at this juncture that the effective emitting area of the cathode was not entirely under control in these experiments. A displacement of a Schottky line parallel to itself can occur either as a result of a change in emitting area or a change of work function. The slope of the line, however, is independent of these factors, and depends only on the dielectric constant, the temperature and absolute constants (except if $p\neq 1$). Thus, while the fact that the curves exhibit a straight line portion plotted in this manner is in itself good proof of the theory, the additional fact that the slope of this line has exactly the correct value, independent of the distance *d* between the electrodes, cannot possibly be attributed to chance agreement. Other attributes of the current, such as its instantaneous response to voltage changes (except with large amounts of adsorbed gases, which diffuse somewhat slowly at room temperature) are also in accord with the theory.

The work function of platinum is about 6 volts, that of nickel about 5 volts. We may therefore expect greater emission from nickel

[11] de Boer, reference 7; also E. K. Rideal, *An Introduction to Surface Chemistry* (Cambridge Press, 1930).

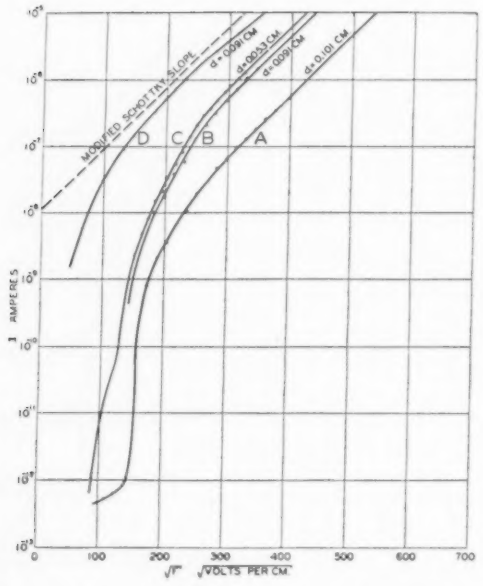

FIG. 6. Current-voltage characteristics for oxygen on nickel. Temperature was 45°C.

than from platinum. In addition, we may expect the work function of nickel to be less influenced by adsorbed hydrogen than that of platinum, as is the case in vacuum, since the adsorbed ions are less firmly bound on nickel than on platinum because of its lower work function.[12]

In Fig. 5, curve *A* was obtained with a nickel electrode that had been heated in hydrogen. It shows the smaller slope characteristic of emission from valleys. Curve *C* was obtained by partially outgassing the electrodes and still shows the effect of hydrogen. Curve *B* was obtained by extreme outgassing over a period of 20 hours. Even though transferred to the apparatus through the air the nickel was partially bare and the curve exhibits the steeper slope due to the presence of points not covered by oxygen.

[12] de Boer, reference 7, p. 151; R. W. Gurney, Phys. Rev. **47**, 479 (1935).

In Fig. 6 curves *A*, *B* and *C* are examples of nickel outgassed to remove hydrogen, and then soaked in oxygen at room temperature. They all show the correct Schottky slope.

Curve *D* in Fig. 6 was obtained by adding iodine to the toluene. In this case the effect of adding iodine may be seen by direct comparison with curve *B*, which represents the condition just previous to the addition. Since iodine is an electronegative element, it should behave in a manner analogous to oxygen and therefore raise the work function, and decrease the current. Instead, the current was increased considerably. This increase may possibly be attributed to the electrolytic deposition of hydrogen on the cathode supplied by the hydroiodic acid liberated by the action of iodine on toluene, which takes place very slowly at ordinary temperatures. The fact that the slope of the high field portion of the curve is less than the theoretical supports this view. The current represented by curve *D*, once established, was independent of the iodine concentration, being unchanged by repeated washing out of the electrode chamber with fresh toluene. It had all of the properties of an electron current. This curve was included particularly to illustrate the large electron currents that are possible even at low fields.

Since we have shown that these electron currents not only impair the insulating qualities of dielectric liquids but can cause chemical deterioration of them as well, the possibility of increasing the work function of electrodes such as the conductor in oil insulated cable, becomes evident. It is curious, in this connection, that the presence of oxygen should appear to be beneficial, since it has long been considered to be harmful because of the danger of oxidation of the organic insulating liquid.

In conclusion the authors wish to express their appreciation of the efforts of the personnel of the research laboratory whose cooperation made this work possible.

Kinetic Energy of Nuclei in the Hartree Model

H. A. BETHE AND M. E. ROSE
Cornell University, Ithaca, New York

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In the present note the question of the separation of the kinetic energy of the center of gravity from the total kinetic energy of the nucleus is considered. This separation is necessitated in the calculation of nuclear energy levels by the use of the Hartree method. It is found that under certain conditions the wave function for the whole nucleus in absolute coordinates can be replaced by a product of the same function of the coordinates of the particles relative to the center of gravity and a 1*s* wave function for the center of gravity. These conditions are that oscillator wave functions be used for the individual particles and that the nucleus contain only one partly filled shell in both protons and neutrons with all shells of lower energy quantum number filled. It then follows that the kinetic energy of the nucleus is equal to the value calculated in absolute coordinates minus the energy of a single 1*s* particle.

IN the calculation of the energy levels of light nuclei from the individual particle model (Hartree approximation), it is the usual procedure to use wave functions in which the nuclear particles are coupled to a fixed point (absolute coordinates) rather than to each other. The kinetic energy T of the nucleus calculated with such wave functions will contain the spurious kinetic energy of the center of gravity which must be deducted. For this purpose several authors have replaced the mass M of a single particle by the reduced mass $M(1-1/N)$ where N is the total number of particles in the nucleus.[1] However, such a procedure is correct only for a two particle problem or for the case that all the particles are in the 1*s* shell. It is our purpose in this note to investigate this point in a somewhat more general case. This investigation, we shall find, is greatly facilitated by the fact that the wave functions ordinarily used, i.e., those in an oscillator potential, actually contain the center of gravity only in a trivial factor. By separating off this factor one obtains directly wave functions containing only relative coordinates.

For the oscillator potential

$$U=-U_0+\tfrac{1}{2}M\omega^2r^2, \tag{1}$$

ω being the frequency of a classical oscillator of mass M (proton or neutron mass) in the field U, the individual particle wave functions in absolute coordinates are:

1*s* level $\psi=ce^{-\alpha r^2}$, (2)

2*p* level $\psi=c'(x, y \text{ or } z)e^{-\alpha r^2}$, (2′)

and in general for "energy quantum number"[2] k,

$$\psi=P_{k-1}(x, y, z)e^{-\alpha r^2}. \tag{2''}$$

Here c and c' are normalization constants, P_{k-1} is a polynomial of degree $k-1$ and

$$\alpha=M\omega/2\hbar. \tag{3}$$

For the wave function Ψ of the whole nucleus we may take a product of two antisymmetric (determinantal) wave functions, one for the neutrons and one for the protons, each determinant being constructed from the spin and space wave functions (2) of the individual particles. In all cases the wave function Ψ will contain the factor $e^{-\alpha\sum_1^N r_i^2}$. This factor may easily be transformed into center of gravity coordinates $\mathbf{R}$ and relative coordinates $\boldsymbol{\varrho}_i$ with respect to that point:

$$\mathbf{R}=\sum_1^N \mathbf{r}_i/N \tag{4}$$

and $$\boldsymbol{\varrho}_i(\xi_i, \eta_i, \zeta_i)=\mathbf{r}_i(x_i, y_i, z_i)-\mathbf{R}(X, Y, Z), \tag{5}$$

writing the Cartesian components of the vectors in the brackets. The relative coordinates $\boldsymbol{\varrho}_i$ are of course not independent but fulfill the relation

$$\sum_1^N \boldsymbol{\varrho}_i=0. \tag{6}$$

[1] Cf., e.g., S. Flügge, Zeits. f. Physik **96**, 459 (1936).

[2] By the energy quantum number k we mean the quantum number which defines the energy of a single particle in the oscillator field. For the field (1) this energy is $E=-U_0+\hbar\omega(k+\frac{1}{2})$. The relation between k and the principal and azimuthal quantum numbers, n and l, is $k=2n-l-1$. See H. A. Bethe and R. F. Bacher, Rev. Mod. Phys. **8**, 82 (1936), §32.

From (5) and (6) it follows that

$$e^{-\alpha\sum_1^N r_i^2}=e^{-\alpha NR^2}e^{-\alpha\sum_1^N \rho_i^2}. \tag{7}$$

We have now to consider the transformation of the determinants in the wave function which remain after the factorization of the gaussian term (7). For the sake of simplicity we shall first consider the case in which, for each kind of particle, the $1s$ shell is complete and the $2p$ shell is partly filled. In this case each determinant will have, in general, the form

$$D(\mathbf{r}_i)=\begin{vmatrix} \alpha_1 & \beta_1 \cdots & x_1\alpha_1 \cdots & y_1\beta_1 \cdots \\ \alpha_2 & \beta_2 \cdots & x_2\alpha_2 \cdots & y_2\beta_2 \cdots \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{vmatrix} \tag{8}$$

in which α and β are the spin wave functions specifying the spin component in a given direction z. Now in D we may add to any column a constant multiple of any other column without changing the value of the determinant. Thus we may add to the $x_i\alpha_i$ column $-X$ times the α_i column and the former column becomes $\xi_i\alpha_i$ by (5). Similarly the $y_i\beta_i$ column can be replaced by $\eta_i\beta_i$ and so on without changing the value of the determinant. It follows therefore that

$$D(\mathbf{r}_i)=D(\boldsymbol{\rho}_i) \tag{9}$$

and from (7) $\quad \Psi(\mathbf{r}_i)=e^{-\alpha NR^2}\Psi(\boldsymbol{\rho}_i). \tag{9'}$

It should be noted that in the derivation of (9) it is essential that the $1s$ shell be complete.[3] It is also true that the separation effected in (9') depends on the properties of the oscillator wave functions in an essential way and this result will be valid only for such wave functions.

The extension of this result to the case of higher shells is obvious. The relations (9) and (9') will be valid in this case if only, for each kind of particle, all the shells of lower energy quantum number[2] be filled.[4] It is sufficient in each case to consider only a single monomial in the polynomial P_k since the determinant with P_k can be written as a sum of determinants in which P_k is replaced by the various monomials. In the transformation of a column containing $x^a y^b z^c$ one gets $\xi^a\eta^b\zeta^c$ plus additional monomials of lower degree. These additional monomials will coincide within a constant factor (powers of X, Y and Z) with elements in one of the columns belonging to a shell of smaller k and therefore give a vanishing contribution to the determinant.

We may now proceed to the calculation of the nuclear kinetic energy. The transformation of the kinetic energy operator in absolute coordinates, $\sum_1^N \Delta_{r_i}$, gives, as is well known, the kinetic energy operator for the center of gravity, $\Delta_{\mathbf{R}}/N$, plus an operator $\Omega_{\boldsymbol{\rho}}$ depending only on the relative coordinates. The operator $\Omega_{\boldsymbol{\rho}}$ is not the sum of the Laplace operators $\Delta_{\boldsymbol{\rho}_i}$ but will contain in addition cross derivatives of the form $\mathrm{div}_{\boldsymbol{\rho}_i}\cdot\mathrm{grad}_{\boldsymbol{\rho}_j}$ because the $\boldsymbol{\rho}_i$ are not independent (Eq. (6)). Therefore it is not simple to calculate the kinetic energy T', exclusive of the energy of the center of gravity, with this operator and the wave function $\Psi(\boldsymbol{\rho}_i)$. However, T' can be easily calculated as the difference between the total kinetic energy in absolute coordinates, T, and the kinetic energy of the center of gravity, T_R. T is the sum of the kinetic energies of the individual particles in the oscillator potential. For the kinetic energy of the center of gravity we have, using (3),

$$T_R=-\frac{\hbar^2}{2MN}\frac{\int d\mathbf{R}e^{-\alpha NR^2}\Delta_{\mathbf{R}}e^{-\alpha NR^2}}{\int d\mathbf{R}e^{-2\alpha NR^2}}=\tfrac{3}{4}\hbar\omega; \tag{10}$$

that is, just the kinetic energy of a single $1s$ particle.

For the kinetic energy T' of a nucleus with all shells (for both particles) of energy quantum number K or less filled and with q particles in the shell of quantum number $K+1$ we find

$$\begin{aligned} T_K' &= \tfrac{1}{4}\hbar\omega\{q(2K+3)-3+\sum_{k=1}^{K}2k(k+1)(2k+1)\} \\ &= \tfrac{1}{4}\hbar\omega\{q(2K+3)-3+K(K+1)^2(K+2)\} \\ &= \tfrac{1}{4}\hbar\omega\{(2K+3)N-3 \\ &\qquad -\tfrac{1}{5}K(K+1)(K+2)(K+3)\}, \end{aligned} \tag{11}$$

in which use has been made of the fact that the total number of particles of both kinds in the

[3] Of course the $1s$ shell for one kind of particle need not be complete if there are no $2p$ particles of this kind. The relation (9) is trivial in the case of only $1s$ particles.

[4] The number of filled neutron shells need not be the same as the number of filled proton shells.

shells with quantum number k is $2k(k+1)$. The case of greatest interest is that in which the $2p$ shell is partly filled and the $1s$ shell complete. In this case $K=1$ and the kinetic energy is

$$T_1'=\frac{\hbar\omega}{4}(5q+9)=\frac{\hbar\omega}{4}(5N-11). \qquad (11')$$

The difference between the result for the kinetic energy obtained here and that resulting from the use of the reduced mass is

$$\Delta T_K'=T_K/N-\tfrac{3}{4}\hbar\omega, \qquad (12)$$

which for $K=1$ is

$$\Delta T_1'=\hbar\omega(N-4)/2N. \qquad (12')$$

This correction varies between 25 and 50 percent of the energy $\frac{3}{4}\hbar\omega$ for the nuclei of mass number between 6 and 16, and will have the effect of raising the energy levels as formerly computed by about 2 to 4 MV for these nuclei.

It is with pleasure that one of us (M. E. Rose) acknowledges his indebtedness to The American Philosophical Society for a grant from the Penrose Fund.

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Spherical Symmetry of Self-Consistent Atomic Fields

A. F. STEVENSON
Department of Applied Mathematics, University of Toronto, Toronto, Canada
(Received November 25, 1936)

THE method of the self-consistent field (s. c. f.) for an N electron atom is equivalent to the assumption

$$\psi=\psi_1(1)\cdots\psi_N(N) \qquad (1)$$

in the variational principle. This leads (neglecting spin terms) to the equations

$$\nabla_j^2\psi_j+(\epsilon_j-2V_j)\psi_j=0 \quad (j=1,\cdots,N), \qquad (2a)$$

where

$$V_j(\mathbf{r}_j)=-Z/r_j+\sum_{k=1(k\neq j)}^{N}\int|\psi_k(\mathbf{r}_k)|^2/r_{jk}\cdot d\tau_k, \qquad (2b)$$

Z being the nuclear charge, and atomic units being used. On the other hand, all calculations which have actually been made so far with the s. c. f. have proceeded on the assumption that the field for each electron is spherically symmetrical. This is effected by making the additional assumption

$$\psi_j(\mathbf{r}_j)=(2\pi)^{-\frac{1}{2}}e^{im_j\phi_j}P_{m_jl_j}(\theta_j)R_j(r_j) \qquad (3)$$

in the variational principle, where we denote by $P_{ml}(\theta)$ the *normalized* tesseral harmonic $P_l^{|m|}(\cos\theta)$, m_j and l_j being the magnetic and azimuthal quantum numbers of the jth electron.

The assumption (3) is, however, incompatible with Eqs. (2a), (2b) unless all the electrons are s electrons. Excluding this special case, therefore, (3) imposes a restriction on the form of the wave function which is *additional* to that implied by (1). Consequently, although the assumption of spherical symmetry is entirely reasonable from the physical point of view and simplifies considerably the numerical work, it would appear that the generalized Eqs. (2) are more accurate than those ordinarily used, and this seems to have been the generally held opinion. If this were really the case, one might solve the more general equations by approximate methods and estimate the magnitude of the corrections that would thereby result. A closer examination, however, leads to the conclusion that if the assumption (1) is made (or the generalizations considered below), the central field assumption is, in effect, a *necessary* one if the solution obtained is to fulfil certain general requirements.

Let us first of all examine the nature of the solution of Eqs. (2). There is a degree of arbitrariness about the solution, but we may safely assume that the central field approximation is a good one. Let us, then, see what type of solution results when we solve (2) by successive approxi-

mations, starting with a definite central field solution (3) (in which the functions R_j are those obtained from the usual Hartree equations) as initial approximation. This may be accomplished by continually substituting the lower order approximation in the expression (2b) for $V_j(\mathbf{r})$. Thus the second approximation is given by substituting (3) (where R_j is regarded as known) in (2b), and then solving Eqs. (2a). Excluding the case of all l's being zero, this makes V_j a function of r_j, θ_j, and the l's and m's of the different electrons, but independent of ϕ_j. Eq. (2a) then has solutions of the form $e^{im\phi_j}f_m(r_j, \theta_j)$, where m is an arbitrary integer. The eigenvalues ϵ_j are non-degenerate, and it is clear that we must take one of the solutions with $m=m_j$.[1] Thus the second approximation is

$$\psi_j(\mathbf{r}_j)=e^{im_j\phi_j}f_{m_j}{}^{(m)}(r_j, \theta_j) \quad (j=1, \cdots, N) \quad (4)$$

and proceeding successively in this way, we see that the final solution is also of the form (4). We indicate by the superscript m that f_{m_j} depends on the m's of all electrons, and not merely on m_j itself. We may expect that $f_{m_j}{}^{(m)}(r_j, \theta_j)$ will not differ very much, however, from the initial central field approximation $P_{m_jl_j}(\theta)_jR_j(r_j)$.

But the solution (4) makes not only the eigenfunctions, but also the eigenvalues ϵ_j and the energy of the whole atom a function of the magnetic quantum numbers m (as well as of the n's and l's). This result is clearly incorrect, and, in fact, renders the solution indeterminate, since m_j may have any integral value between $\pm l_j$. To obtain a result for the energy which is independent of the m's, it is therefore necessary to *average* over the m's. But the assumption (3) (with the R's assumed independent of the m's) *is* compatible with the equations (2) if the potentials V_j are averaged in this way; for each term in the summation in (2b) is then of the form

$$1/2\pi\int(1/r_{jk})(2l_k+1)^{-1}\sum_{m_k=-l_k}^{l_k}[P_{m_kl_k}(\theta_k)]^2 \cdot[R_k(r_k)]^2d\tau_k$$

and the summation with respect to m_k has just the value $(2l_k+1)/2$,[2] so that we have

$$[V_j(\mathbf{r}_j)]_{\text{av}}=-Z/r_j + 1/4\pi\sum_{k=1(k\neq j)}^{N}\int[R_k(r_k)]^2/r_{jk}\cdot d\tau_k,$$

which is a function of r_j only, so that the assumption (3) is permissible, and we obtain, in fact, just the Hartree equations for the radial functions. It may be noted that such an averaging over magnetic quantum numbers is necessary even when the restriction (3) is made *before* applying the variational principle, in order to obtain the Hartree equations.[3] It is true that we might perform the averaging *after* solving Eqs. (2) (in the form (4)) rather than before; but it is very doubtful if this would improve the result, and the process of solution would, of course, be much more laborious.

The dependence of the solution on the magnetic quantum numbers m is, of course, due to the spatial degeneracy of the central field solution (3), and we might try to correct for this, while still retaining essentially the s. c. f. method, by assuming for the wave function a linear combination of products of the form (cf. (4))

$$\prod_{j=1}^{N}e^{im_j\phi_j}g_{m_j}(r_j, \theta_j) \quad (5)$$

for the different possible values of the m's, i.e., for $m_j=-l_j, \cdots, l_j$. The functions g_{m_j} (not necessarily identical with the f_{m_j} considered above) would then be determined by the variational principle. In this case, we must certainly impose the condition that the wave functions belonging to a given state of the whole atom must have the correct transformation properties with respect to change of axes.[4] We may first suppose the g_{m_j} in (5) expanded in the form

$$g_{m_j}(r_j, \theta_j)=\sum_{p_j=|m_j|}^{\infty}A_{m_jp_j}(r_j)P_{m_jp_j}(\theta_j).$$

Now it is impossible to find linear combinations

[1] *Which* eigenvalue is to be taken could be fixed by consideration of the initial approximation (thus introducing the principal quantum numbers of the different electrons). We might, e.g., employ the method given by the author (Trans. Roy. Soc. Canada **30**, 75 (1936)) for solution of (2a) (with V_j known) by successive approximations, starting with (3) as initial approximation.

[2] See, e.g., Sommerfeld, *Wellenmechanischer Ergänzungsband* (1929), 103.

[3] Condon and Shortley, *Theory of Atomic Spectra* (1935), 356.

[4] See, e.g., Wigner, *Gruppentheorie, etc.* (1931).

of products of the form

$$\prod_{j=1}^{N} e^{im_j\phi_j} P_{m_j p_j}(\theta_j)$$

with the *same* coefficients (in the linear combination) for *different* values of the p_j which transform in the correct manner under a rotation of axes; so that the only possibility of finding linear combinations of functions of the form (5) which have the correct transformation properties and which tend continuously to the correct wave functions as the electronic interaction be imagined to tend to zero, is to take

$$g_{m_j}(r_j, \theta_j) = \text{const.} \times R_j(r_j) P_{m_j l_j}(\theta_j), \qquad (6)$$

where R_j is independent of the m's. We then have wave functions of the form

$$\psi_M{}^L = \prod_{j=1}^{N} R_j(r_j) \cdot \sum_{m_1, \cdots, m_N} C(L, M; m_1, \cdots, m_N) \times \prod_{j=1}^{N} e^{im_j\phi_j} P_{m_j l_j}(\theta_j) \qquad (7)$$

belonging to a given L state of the whole atom, where M goes from $-L$ to L, and in the summation m_1 goes from $-l_1$ to l_1, etc. The constants C are then independent of the electronic interaction, and are, in principle, determinable from group-theoretical considerations alone.[4]

It thus appears that any wave functions which are built up as linear combinations of functions such as (5) *without* the "central field" assumption (6) do not have the correct transformation properties, and are therefore to be rejected. Application of the variational principle with the wave function (7) yields equations for the radial functions R which differ slightly from those of Hartree in that the field for each electron is different for the different states arising from the same electronic configuration. The corrections obtained in this way, however, are of about the same order of magnitude as the exchange corrections, so that there is no point in taking them into account without at the same time including the exchange corrections.[5]

In all the above we have neglected exchange degeneracy and the Pauli principle; but even if we take these into account, the conclusion regarding the necessity for central fields remains valid. For the correct wave function may be obtained by first solving the wave equation when exchange degeneracy and spin are neglected, and then forming linear combinations of this solution and its various permutations, the coefficients being appropriate spin functions. But these spin functions are again independent of the electronic interaction and are determinable from group-theoretical considerations alone. It is therefore sufficient to study, in the first place, those approximate wave functions which neglect spin and exchange degeneracy, and our previous conclusion remains true. The generalization of (7) to include exchange and the Pauli principle then yields, when the variational principle is applied, precisely the radial equations of the s. c. f. with exchange.[5]

[5] Cf. Slater, Phys. Rev. **35**, 210 (1930). The difference between the Hartree equations and those considered here is due to the fact that in the former the wave function assumed in the variational principle does not have the proper transformation properties. This is not so, however, in the equations of the s. c. f. with exchange (see, e.g., Hartree and Hartree, Proc. Roy. Soc. **A154**, 588 (1936)). This point is discussed more fully for two-electron configurations in a paper (not yet published) of the writer, where a generalization of the s. c. f. equations is also given.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the eighteenth of the preceding month; for the second issue, the third of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Communications should not in general exceed 600 words in length.

On the Anomalous Diffraction Gratings. II

In my former letter on this question[1] I have pointed out that, if one considers the presence of Sommerfeld's surface waves on a grating, one may explain the part (*b*) of the "typical phenomenon" of Wood and Strong. The introduction of these waves was physically justified but quite arbitrary from the point of view of the mathematical formalism. Owing in particular to critical discussion with Professors Laue and Sommerfeld, to whom I am very indebted, I have now attempted to overcome the mathematical difficulties.

Sommerfeld's method, to find the field of an oscillator on a metallic surface, consists in developing this field in a Fourier integral of cylindrical waves. A particular transformation of this integral shows that the superficial part of the field is represented by a superficial damped wave. Following this method I have represented the complex of reflected, refracted and diffracted waves in the theory of the metallic gratings as a Fourier integral of plane waves. Rayleigh's theory follows then automatically without a naive application of the principle of Huygens.

It was only on this point that I noted that the bright bands, part (*b*) of the "typical phenomenon," are already given by developing the method of Rayleigh and Voigt. These bands are due to the same particularity in the mathematical formalism as Sommerfeld's superficial waves; they have their center at the same wave-length as that which corresponds to the resonance of Sommerfeld's waves when we represent the grooves of the grating as a series of harmonic resonators. I may also say that, although I had not seen the simple mathematical aspect of the experimental phenomenon, the explanation which is given in my former work was physically correct.

In Rayleigh's work the metal is thought to be perfectly conducting; then the intensity of a continuous diffraction spectrum, as a function of the wave-length, becomes infinite at Rayleigh's wave-lengths, and so does its first derivative. When the conductivity is not infinite this singularity breaks down into two parts: (*a*) the derivative remains infinite at Rayleigh's wave-lengths, (*b*) the intensity becomes finite and has a wide and displaced maximum.

In conclusion I wish to summarize the exact meaning of the results obtained, which seem now to be satisfactory. We may calculate the complex amplitudes (functions of the wave-length) of the diffracted waves in a continuous spectrum as a series of ascending powers of the depth of the grooves. One of the terms of second order: (*a*) is discontinuous at Rayleigh's wave-lengths, (*b*) has a wide maximum—in its absolute value—for slightly larger wave-lengths. The qualitative and quantitative influence of these irregularities on the resulting intensity of the spectrum depends very largely upon the profile of the grating as pointed out in the former letter.

A complete account will be published in the *Annalen der Physik*.

UGO FANO

Torino, Italy,
January 1, 1937.

[1] Fano, Phys. Rev. **50**, 573 (1936).

The Infrared Absorption of the Hydrogen Halides in Organic Solvents

The appearance of the interesting papers by West and his colleagues on the infrared and Raman spectra of simple gases in nonionizing solvents[1, 2] has suggested to the writer the propriety of recounting his observations on the infrared absorption of hydrogen bromide and hydrogen iodide in organic solvents, made in continuance of work on the spectra of hydrogen chloride solutions.[3, 4] In the case of the aromatic solvents, chlorobenzene, nitrobenzene, and *m*-nitrotoluene, the solubility of HBr and HI is so slight that no definite conclusions could be drawn concerning the absorption of the solute, although it appears that the fundamental frequencies are lower than in the gas. In benzene solution the fundamental bands of HBr and HI appear at 3.9 μ and 4.5 μ, respectively, the absorption maximum not differing appreciably from that of the free gases. The observations on the iodide solutions had to be made immediately after the solutions were prepared, since the solute decomposes very rapidly. The HBr solutions offered similar difficulties, but the decomposition took place more slowly. In the case of every solution studied, the absorption coefficient of the dissolved gas was greater than that of the free gas. The absorption of HCl was found to be more intense than that of HBr and HI, a result to be expected from the studies made on these compounds in the gaseous state. The studies have been extended to include solutions of HCl, HBr and HI in ether, in which solvent a high degree of ionization is known to occur. In each ether solution the bands characteristic of the solute were entirely absent, a result in accord with West's observations. As yet no work has been done on solutions of hydrogen fluoride.

DUDLEY WILLIAMS

University of Florida,
Gainesville, Florida,
January 28, 1937.

[1] W. West and P. Arthur, J. Chem. Phys. **5**, 10 (1937).
[2] W. West and R. T. Edwards, J. Chem. Phys. **5**, 14 (1937).
[3] E. K. Plyler and D. Williams, Phys. Rev. **49**, 215 (1936).
[4] D. Williams, Phys. Rev. **50**, 719 (1936).

Some Generalizations of the β Transformation Theory

According to a hypothesis of Pauli, worked out in detail by Fermi and others,[1] the emission of an electron in the process of β transformation must be accompanied by simultaneous emission of a neutrino in order to satisfy the conservation of spin and energy ($n \rightarrow p + e^+ + \nu$ or $p \rightarrow n + e^- + \nu$). We should like to discuss here the possibility of two other similar processes: *The emission of a pair of electrons* ($n \rightarrow n + e^+ + e^-$ or $p \rightarrow p + e^+ + e^-$) and *the emission of a pair of neutrinos* ($n \rightarrow n + \nu + \nu$ or $p \rightarrow p + \nu + \nu$). Such processes evidently do not correspond to nuclear transformations though they could occur together with γ-radiation if the nucleus is excited.

These processes may be of importance for the explanation of forces between heavy particles and also their magnetic moments. In principle, such an explanation was given[2] on the basis of (e, ν) pair emission (ordinary β transformation); however, for both effects the calculated results (accepting U–K interaction) were too small by a factor of about 10^{12}. Considering the interaction forces and magnetic moments as due to (e^+, e^-) or (ν, ν) pair emission, however, we can obtain the correct values, since we have considerable freedom in choosing the probabilities for these new processes. We shall ascribe the above two effects to (e^+, e^-) emission because, in order to give a reasonable explanation of magnetic moments of heavy particles, the momentary emission of pairs possessing sufficiently large magnetic momenta is needed.

In the case of (e^+, e^-) emission (and also (ν, ν) emission) the charge of the heavy particle remains unchanged, although the spin may change. This seems to correspond to the fact that *forces between heavy particles depend on their spins but not on their charges*. Indeed, experimental evidence shows that the (n, p) and (p, p) forces are equal if the spins of two particles are antiparallel.[3] The (n, p) force for parallel spins is an attraction and we conclude that the same is true for the (p, p) force. Thus, apart from Coulomb forces, *attraction between any pair of heavy particles* results. If we furthermore assume that the total potential energy of a nucleus is a sum of interaction energies of separate pairs, then, owing to *the absence of valency saturation* for our type of exchange-phenomena, heavy nuclei would collapse to a radius comparable with the range of forces between constitutional particles.[4] Therefore, we must assume that the *interaction between two particles must be affected (reduced) by the presence of other particles*. If *several pairs may be exchanged simultaneously between two or several heavy particles*,[5] such an effect can be easily understood. It has been shown by perturbation calculations that a perturbing potential which leads to a correct magnitude of interaction gives rise to high order perturbations which converge rather slowly;[6] from this it follows that the above-mentioned simultaneous exchange of several pairs may possess a considerable probability. Assuming that the probability of (e^-, e^+) transformation is 10^{12} times larger than the probability of the ordinary (e, ν) transformation, *attractive forces and magnetic moments can be described quantitatively*. This assumption would also lead to (e^-, e^+) *pair emission from excited nuclei*, which process would compete with the γ-ray emission whenever the excitation energy exceeds 2 mc^2. If the (e^-, e^+) pair is emitted with one mv total kinetic energy, the probability would be 10^9 sec.$^{-1}$ ($10^{12} \times \beta$ decay constant for this energy) which, for heavy nuclei, is comparable with the probability of the Dirac pair formation by γ-rays in the vicinity of the emitting nucleus.[7]

It seems reasonable to expect that the ratio of the probabilities of (ν, ν) and (ν, e) emissions is of the same order of magnitude as for (ν, e) and (e^+, e^-) emission. This would lead to comparable probabilities for (ν, ν) pair emission and for the emission of quanta of gravitational radiation.[8]

G. GAMOW
E. TELLER

George Washington University (GG and ET),
Carnegie Institution of Washington (GG),
Washington, D. C.,
January 19, 1937.

[1] E. Fermi, Zeits. f. Physik **88**, 161 (1934); G. Uhlenbeck and K. Konopinski, Phys. Rev. **48**, 7 (1935).
[2] D. Iwanenko and I. Tamm, Nature **133**, 981 (1934); C. Wick, Rend. R. Nat. Acad. **21**, 170 (1935); C. Weizsäcker, Zeits. f. Physik **102**, 572 (1936).
[3] M. A. Tuve, L. R. Hafstad, and N. P. Heydenburg, Phys. Rev. **50**, 806 (1936); G. Breit, E. Condon, and R. Present, Phys. Rev. **50**, 825 (1936).
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[5] D. Iwanenko and A. Sokolow, Nature **138**, 684 (1936); L. and G. Nordheim, Phys. Rev. (in press).
[6] H. Bethe and R. Bacher, Rev. Mod. Phys. **8**, 82 (1936).
[7] R. Oppenheimer and M. Plessett, Phys. Rev. **44**, 53 (1933).
[8] A. Einstein, Berlin, Sitzber. Akad. Wiss. 688 (1918).

Isotopic Constitution of Neodymium

In a previous paper an example of a mass spectrum obtained from a mixture of rare earth elements was given.[1] This included masses at 148 and 150 which could not be identified with any known isotopes. Dr. Aston has suggested[2] that they are new isotopes of neodymium. I have recently analyzed the ions from a spark between fairly pure neodymium electrodes, and find that the masses at 148 and 150 belong to this element (Fig. 1). The faint mass at 141

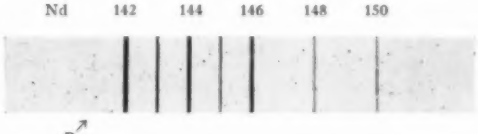

FIG. 1. Mass spectrum of neodymium.

is probably due to a trace of praseodymium. No other impurities were found.

Samarium ions were obtained from sparks to an electrode made by filling a nickel tube with a mixture of samarium oxide and aluminum. The isotopic constitution was found to be the same as that observed by Dr. Aston with the abnormal intensity relationships among the isotopes reported by him.

A. J. DEMPSTER

Ryerson Physical Laboratory,
University of Chicago,
Chicago, Illinois,
February 1, 1937.

[1] Proc. Am. Phil. Soc. **75**, 735 (1935).
[2] F. W. Aston, Nature **137**, 613 (1936).

Nebulae as Gravitational Lenses

Einstein recently published[1] some calculations concerning a suggestion made by R. W. Mandl, namely, that a star B may act as a "gravitational lens" for light coming from another star A which lies closely enough on the line of sight behind B. As Einstein remarks the chance to observe this effect for stars is extremely small.

Last summer Dr. V. K. Zworykin (to whom the same idea had been suggested by Mr. Mandl) mentioned to me the possibility of an image formation through the action of gravitational fields. As a consequence I made some calculations which show that extragalactic *nebulae* offer a much better chance than *stars* for the observation of gravitational lens effects.

In the first place some of the massive and more concentrated nebulae may be expected to deflect light by as much as half a minute of arc. In the second place nebulae, in contradistinction to stars, possess apparent dimensions which are resolvable to very great distances.

Suppose that a distant globular nebula A whose diameter is 2ξ lies at a distance, a, which is great compared with the distance D of a nearby nebula B which lies exactly in front of A. The image of A under these circumstances is a luminous ring whose average apparent radius is $\beta=(\gamma_0 r_0/D)^{\frac{1}{2}}$, where γ_0 is the angle of deflection for light passing at a distance r_0 from B. The apparent width of the ring is $\Delta\beta=\xi/a$. The apparent total brightness of this luminous ring is q times greater than the brightness of the direct image of A. In our special case $q=2la/\xi D$, with $l=(\gamma_0 r_0 D)^{\frac{1}{2}}$. In actual cases the factor q may be as high as $q=100$, corresponding to an increase in brightness of five magnitudes. The surface brightness remains, of course, unchanged.

The discovery of images of nebulae which are formed through the gravitational fields of nearby nebulae would be of considerable interest for a number of reasons.

(1) It would furnish an additional test for the general theory of relativity.

(2) It would enable us to see nebulae at distances greater than those ordinarily reached by even the greatest telescopes. Any such *extension* of the known parts of the universe promises to throw very welcome new light on a number of cosmological problems.

(3) The problem of determining nebular masses at present has arrived at a stalemate. The mass of an average nebula until recently was thought to be of the order of $M_N=10^9\,M_\odot$, where $M_\odot$ is the mass of the sun. This estimate is based on certain deductions drawn from data on the intrinsic brightness of nebulae as well as their spectrographic rotations. Some time ago, however, I showed[2] that a straightforward application of the virial theorem to the great cluster of nebulae in Coma leads to an average nebular mass four hundred times greater than the one mentioned, that is, $M_N'=4\times10^{11}M_\odot$. This result has recently been verified by an investigation of the Virgo cluster.[3] Observations on the deflection of light around nebulae may provide the most direct determination of nebular masses and clear up the above-mentioned discrepancy.

A detailed account of the problems sketched here will appear in *Helvetica Physica Acta*.

F. ZWICKY

Norman Bridge Laboratory,
California Institute of Technology,
Pasadena, California,
January 14, 1937.

[1] A. Einstein, Science **84**, 506 (1936).
[2] F. Zwicky, Helv. Phys. Acta **6**, 124 (1933).
[3] Sinclair Smith, Astrophys. J. **83**, 23 (1936).

Emergence of Low Energy Protons from Nuclei

In some experiments recently described[1] the emission of protons in alpha-particle induced transmutations has been studied. In several cases the interesting fact was noticed that protons of relatively low energy were emitted in considerable numbers. Thus for each of the reactions

$$\begin{aligned}
&Al^{27}+He^4\rightarrow Si^{30}+H^1,\\
&P^{31}\ +He^4\rightarrow S^{34}\ +H^1,\\
&Cl^{35}+He^4\rightarrow A^{38}+H^1,\\
&Ca^{40}+He^4\rightarrow Sc^{43}+H^1,
\end{aligned}$$

a group of protons of maximum range 20 cm or less is found and the yield is in general large (more than one-third of the total number of protons emitted). In each case protons of range 10 cm are observed with no apparent diminution of the probability of emission. The question arises as to how these low energy protons get out of the composite nucleus.

In recent experiments in this laboratory the excitation curve for the emission of neutrons from argon under alpha-particle bombardment has been plotted and the nuclear radius found to be 7.3×10^{-13} cm which is in accord with Bethe's revised radii for the radioactive elements[2] and may be taken as a basis for calculation of the nuclear radii of Si^{30}, S^{34}, A^{38}, Ca^{42} and Sc^{43}. Other evidence (e.g., scattering experiments) indicates, if anything, smaller radii than those found in this way. In Table I are given the radii so calculated, together with the heights of the corresponding proton barriers and the range of a proton just able to surmount them. It will be seen that in every case the experimentally observed ranges are smaller than necessary to scale the barrier. It therefore appears that we can draw one of two significant conclusions from the experimental data. Either *barriers to emerging protons are abnormally low* or *the composite nucleus containing the final product element and the proton has a finite lifetime sufficiently long to enable the proton to leak through the barrier*. The latter view, which is in accordance with Bohr's conception of transmutation,[3]

TABLE I.

Product Nucleus	Nuclear Radius ($\times10^{13}$cm)	Proton Barrier Height (Mev)	Range to Scale Barrier (cm)	Experimentally Found Range
Si^{30}	6.7	3.0	14.0	<10
S^{34}	6.9	3.3	16.5	<10
A^{38}	7.2	3.6	19.0	<10
Ca^{42}	7.4	3.9	22.0	14
Sc^{43}	7.5	4.0	23.0	<10

seems to give the simplest explanation consistent with the remainder of our knowledge about nuclei. It is of some interest to estimate the lifetime of the composite Ti^{44} nucleus formed in the last reaction. This is found to have a minimum value of approximately 10^{-20} second, but it is probably much longer as it may be that protons of much smaller range than have been detected are actually emitted.

ERNEST POLLARD

Sloane Physics Laboratory,
Yale University,
New Haven, Connecticut,
February 2, 1937.

[1] E. Pollard and C. J. Brasefield, Phys. Rev. **50**, 890 (1936); **51**, 8 (1937).
[2] H. Bethe, Phys. Rev. **50**, 977 (1936).
[3] The idea is developed in some detail by W. D. Harkins, Phys. Rev. **51**, 52 (1937).

Cyclotron Operation without Filaments

With the use of a transmission line[1] to supply high frequency power to the dees of a cyclotron, it is possible to operate with a continuous glow discharge in the vacuum chamber. Under these conditions it is unnecessary to use filaments to create ions for acceleration since the high frequency discharge supplies them. In this way we have obtained a steady ion beam current of 5 microamperes. The operating conditions are very stable and the maximum beam current may be drawn for any desired length of time.

Fig. 1 shows a typical curve relating pressure in the vacuum chamber and ion current drawn from the cyclotron under the above conditions. The end of the curve shows the pressure at which the discharge ceased for that particular run. The optimum pressure is of the order of 10^{-6} mm Hg. At lower pressures it is necessary to use filaments to obtain a beam from the cyclotron. An increase in pressure from about 10^{-7} mm Hg up to the above point increases the beam current when using filaments. With filaments the maximum steady beam we have been able to get is 8 microamperes.

When operating without filaments, the pressure is increased to about 10^{-3} mm Hg where the h.f. potential strikes the discharge. The excess gas is then pumped out until the beam is a maximum and steady operating conditions are obtained. The beam current under these conditions, as well as when using filaments, increases with an increase in power transmitted to the dees.

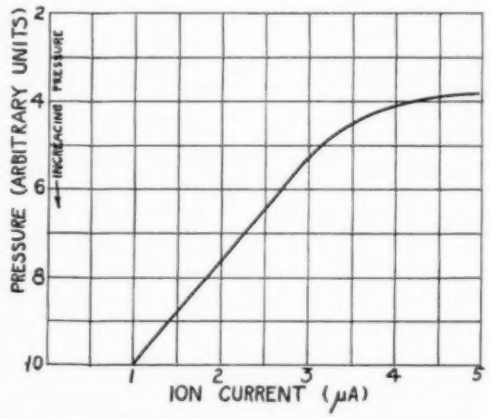

FIG. 1. Relation between gas pressure and ion beam current.

The operating conditions with a continuous glow discharge in the vacuum chamber are much more stable than with no glow discharge, since a small change in gas pressure does not affect the tuning of the dee circuit appreciably. When bursts of gas occur the line impedance match is destroyed and the power delivered to the dees decreases for a short time, but the pumps soon reestablish the proper pressure conditions whereupon the power delivered to the dees and the beam current go up to normal again.

P. GERALD KRUGER
G. K. GREEN
F. W. STALLMANN

Department of Physics,
University of Illinois,
Urbana, Illinois,
January 27, 1937.

[1] Green and Kruger, Phys. Rev. **51**, 57 (1937).

Asymmetric Zeeman Effect Patterns in a Complex Spectrum

Zeeman effect analysis of an atomic spectrum usually shows each energy level to be split symmetrically about its field-free value. Asymmetry has hitherto been recognized (neglecting hyperfine structure) only in LS coupling spectra and certain especially simple two-electron configurations.[1] In these special cases the wave number contribution $o_H Mg$ to a sublevel due to the external field can be made to attain the same order of magnitude as that due to spin-orbit interaction if the latter is sufficiently small (Paschen-Back effect). Here g is the weak field Zeeman effect splitting factor, M is the magnetic quantum number, and $o_H c$ is the Larmor precession frequency.

This limitation of the known asymmetrically split levels to simple spectra, is due to the accidental lack of known level groups sufficiently close to show the interaction, in the more complex spectra that have been magnetically analyzed. In addition to the well-known symmetric splitting term $o_H Mg$, each of the sublevels with the same M value, of any two neighboring levels of the same parity whose J values differ by not more than one, may be expected to have in the expression for its wave number, a repulsion term with the resonance denominator $D=\nu_a-\nu_b+o_H M(g_a-g_b)$. Here g_a, g_b are the weak field g values and $hc\nu_a$, $hc\nu_b$ the field-free energies of the levels. This term equals

$$\begin{array}{lll} Ko_H{}^2M/D & \text{if} & J_a-J_b=0; \\ Ko_H{}^2(J^2-M^2)/D & \text{if} & |J_a-J_b|=1; \\ 0 & \text{if} & |J_a-J_b|>1. \end{array}$$

Here K is a constant characteristic of the pair of levels, and in the case $|J_a-J_b|=1$, J is the larger of the two values J_a, J_b. The expressions are approximate. Levels with $|J_a-J_b|>1$ may be expected to show some repulsion, associated with the fact that J is not a good quantum

number in a magnetic field; but if the repulsion is sufficiently small it may be hard to detect, and experiment may show sublevels with the same M crossing.

The spectrum of neutral tungsten[2] is rich in levels about which nothing is known except parity, ν, J, g, and transition intensities. Lacking *a priori* knowledge of the value of K, we have used the magnitude of o_H^2/D in all cases where $|J_a - J_b| = 0$ or 1 as a measure of the expected nonlinear contribution to the energy of a sublevel.[3] Although there are several pairs a good deal closer, the pair $21{,}448.66_2(1.3)$, $21{,}453.76_1(2.56)$—the data are given in the form $\nu_J(g)$ for each level—shows by far the largest expected nonlinear contribution within the range of field strengths ordinarily attainable for Zeeman effect studies. For the $M=-1$ sublevels of this pair, o_H^2/D equals 0.26 cm^{-1} when $o_H=1$ cm^{-1} (i.e., in an external field of $21.4\cdot10^3$ gauss) and 1.6 cm^{-1} in twice as great a field. For $o_H=4$ cm^{-1}, D would be zero, i.e., the sublevels would cross if the repulsion term were absent. The level 21,453 happens to be one of the very few in the whole spectrum to which one may at present assign some partly meaningful quantum numbers other than J. It acts in some respects as though it deserved the name $5d^46s6p\ {}^5P_1$. "Multiplet separations" in tungsten are of the order of thousands of units. It is not easy to see how 21,448 and 21,453 could be very closely related dynamically.

Of the 657 tungsten lines whose Zeeman effect patterns are listed in the highly consistent work of Jack,[4] many lines are listed with asymmetries of intensity, but only seven with asymmetries of position. Three of the asymmetric pattern measurements may be explained easily as due to faintness or overlapping of complicated patterns; one belongs to a doubly classified line; one is still unclassified. The remaining two (ν22,003 and ν18,128) belong, respectively, to the levels 21,448 and 21,453. Both patterns are incomplete. They appear to afford definite evidence of interaction, with asymmetries on the order of 0.1 cm^{-1} in a field for which $o_H=1.072$ cm^{-1}. Of course this has spoiled the g value determinations, so the values 1.3, 2.56 listed above are not the true weak field g values. Quantitative analysis has been postponed pending the availability of better patterns. An attempt is being made to obtain such patterns.

We are indebted to Professor Breit for a discussion of the problem.

J. E. MACK

University of Wisconsin,
Madison, Wisconsin.

O. LAPORTE

University of Michigan,
Ann Arbor, Michigan,
January 22, 1937.

[1] For a summary see Condon and Shortley, *Theory of Atomic Spectra*, §5, reference 16.

[2] O. Laporte and J. E. Mack, forthcoming publication.

[3] Equally justifiable would have been the procedure of using o_H^2M/D where $J_a - J_b = 0$ and $o_H^2(J^2-M^2)/D$ where $J_a - J_b = 1$. This would have favored the pairs $37{,}297.5_6$, $37{,}309.13_5$ and $40{,}463.1_4$, $40{,}476.37_5$. Actually the (unresolved) patterns of the lines from these levels are listed as being symmetric. In these cases at least, K must be of the order of $1/J^2$ or smaller.

[4] R. Jack, diss. Göttingen 1908; Ann. d. Physik **28**, 1032 (1909).